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Title: Colloidal Semiconductor Nanocrystals: Surface Chemistry, Photonics, and Electronics

Author(s): Fedin, Igor

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Colloidal Semiconductor Nanocrystals: Surface Chemistry, Photonics, and Electronics

Igor Fedin

Research seminar at Rutgers University
Department of Chemistry and Biochemistry

20 February 2020

Acknowledgement

Los Alamos National Laboratory

Chemistry Division

Physical Chemistry and
Advanced Spectroscopy Group

Team of Dr. Victor I. Klimov

The Univerity of Chicago

Department of Chemistry

Group of Prof. Dmitri V. Talapin

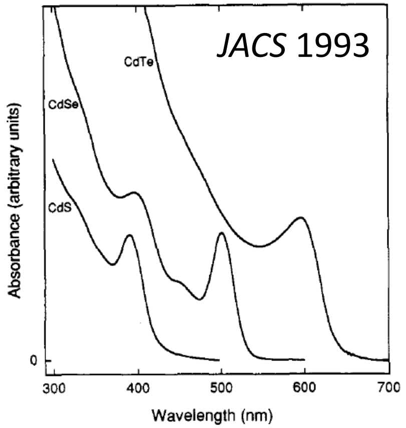
Argonne National Laboratory

Center for Nanoscale Materials

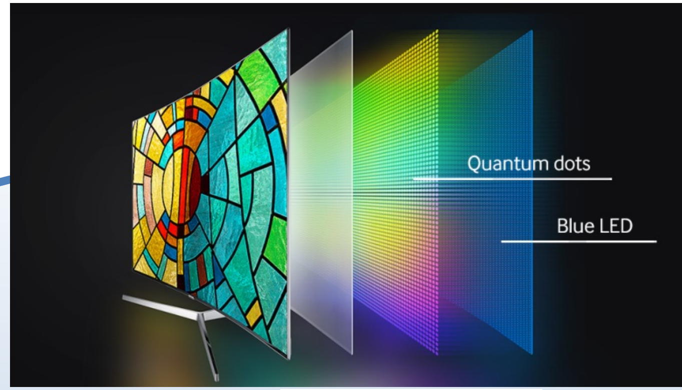
Team of Dr. Richard D. Schaller

Introduction: colloidal quantum dots in photonics

Started three decades ago

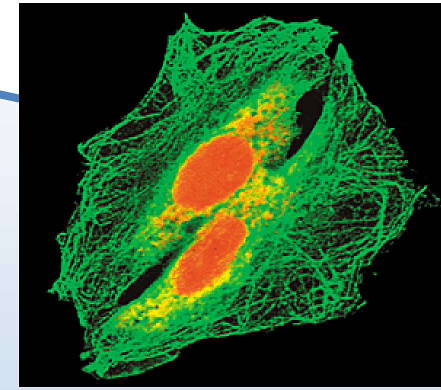


QD displays

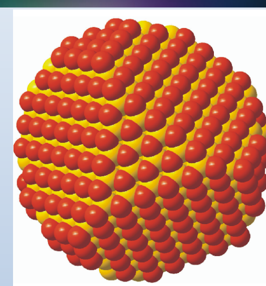


Samsung

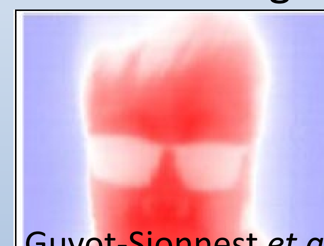
Biological imaging



Qdot website

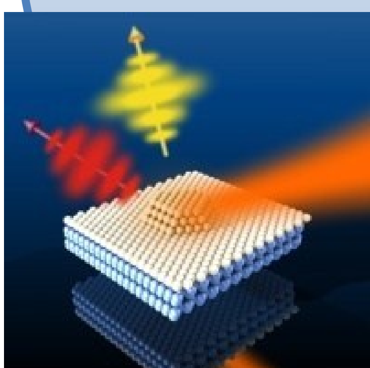


Infrared imaging

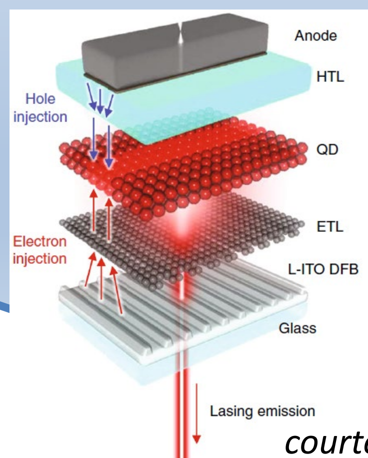


Guyot-Sionnest *et al.* *Nat. Photonics* 2019

Single-photon sources

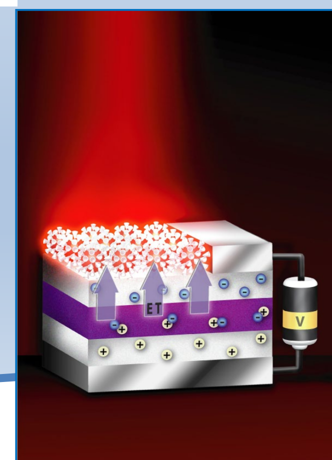


QD lasers



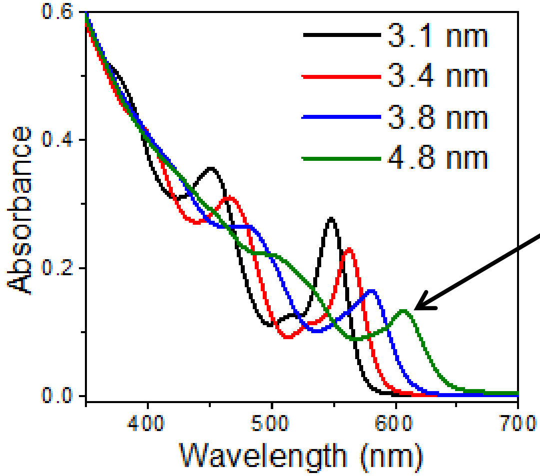
courtesy of V. Klimov

LEDs

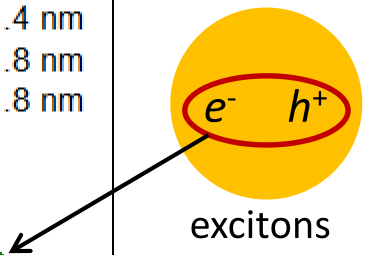


Merits of colloidal quantum dots

Quantum confinement

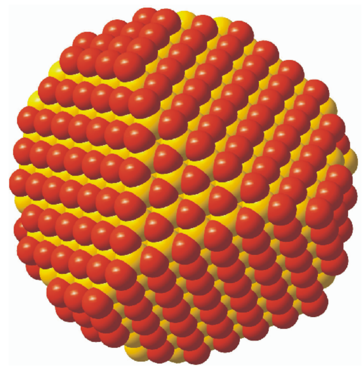


Absorption spectra of CdSe QDs



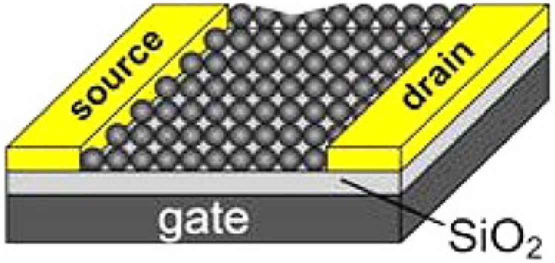
excitons

Photoluminescence



Solution-processability

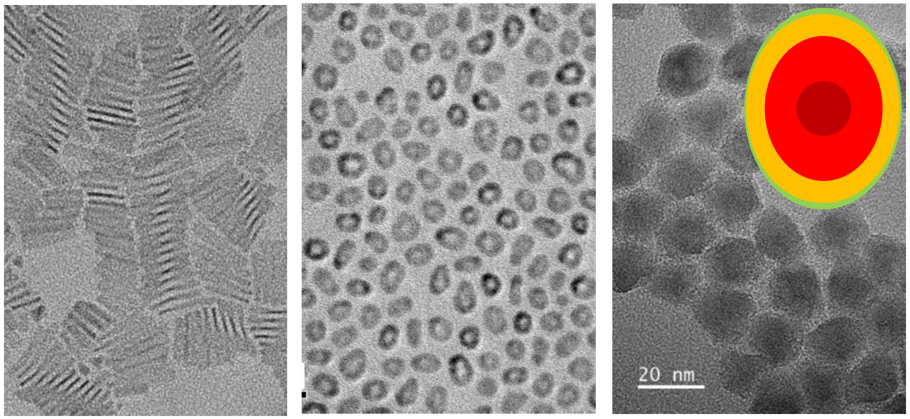
Electrical conductivity



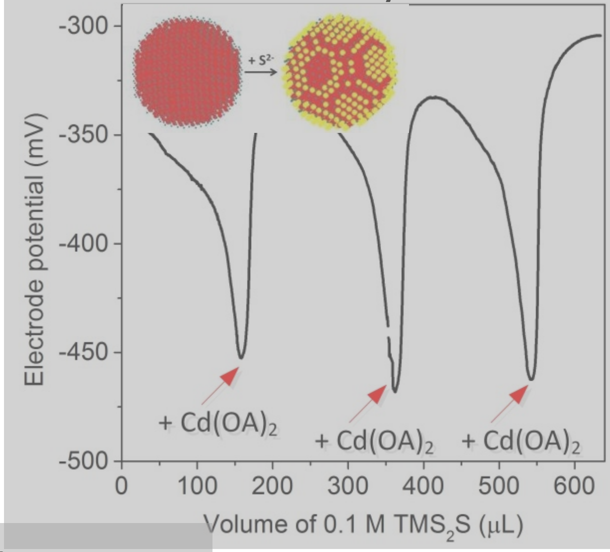
A field-effect transistor (FET) of QDs

Outline

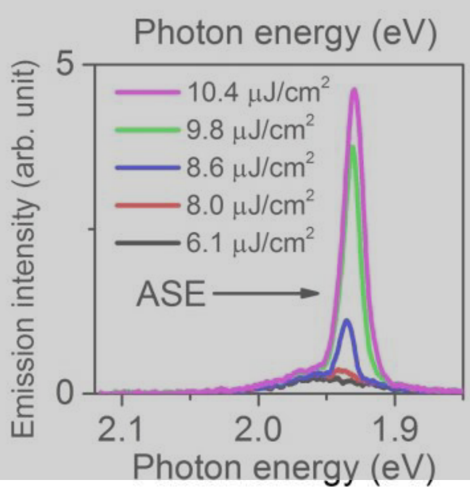
Synthesis of complex heterostructures

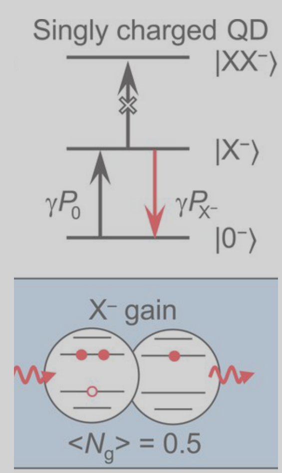


Surface chemistry of colloidal nanocrystals



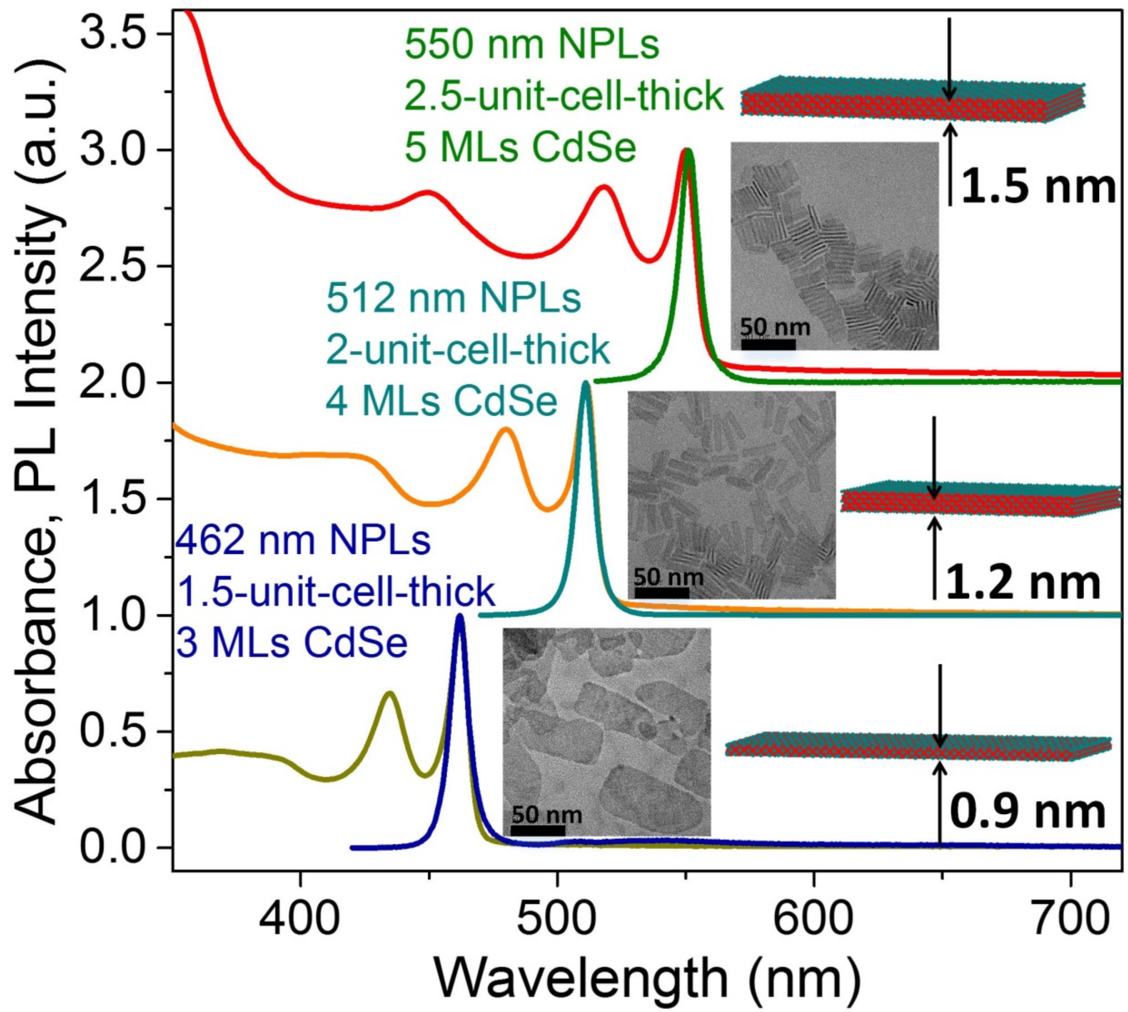
Photonics of CdSe QDs and NPLs: ASE, lasing, and FRET



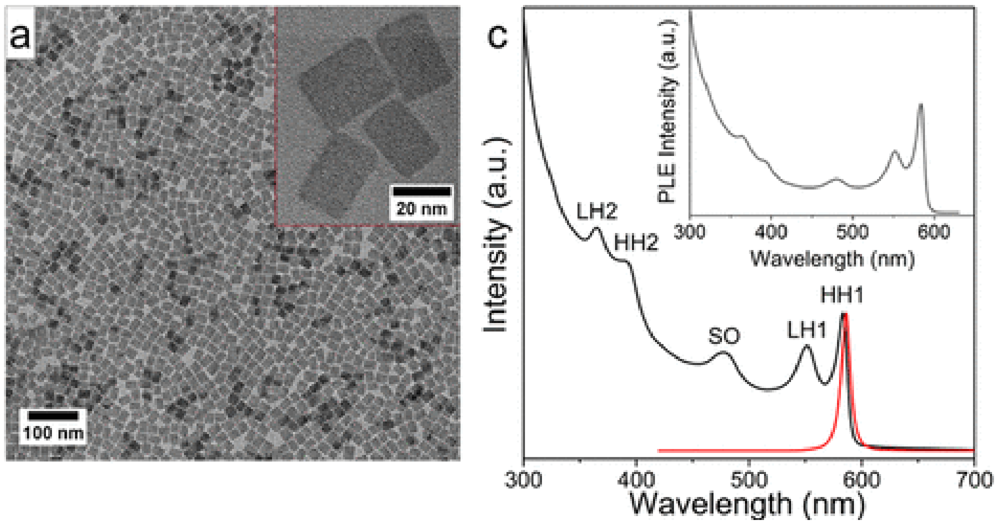


Colloidal zinc-blende CdSe nanoplatelets

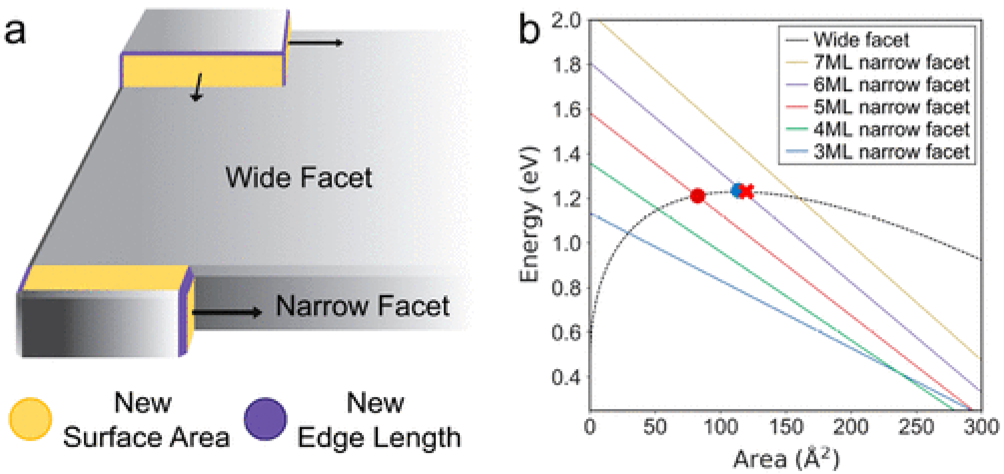
$$Cd(C_{13}H_{27}COO)_2 + Se/ODE \xrightarrow[240^{o}C]{Cd(CH_3COO)_2} CdSe + \ldots$$



The next thickness of CdSe NPLs



Introduction of water or chloride into the synthesis yields 6 ML CdSe NPLs.



The standard reaction:

$Cd(CH_3COO)_2$ + “H_2Se” → CdSe + $2CH_3COOH$

A less favorable reaction:

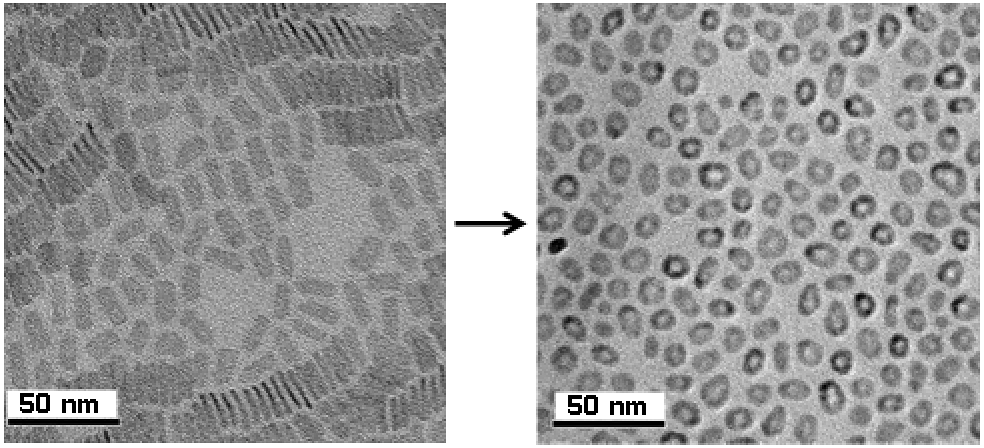
$CdCl_2$ + “H_2Se” → CdSe + 2HCl

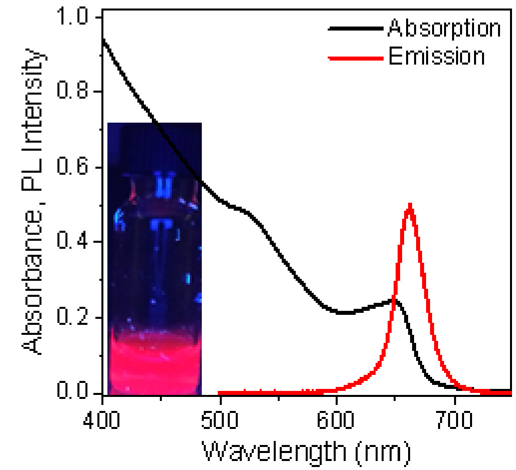
– favors nucleation on the side, and enables formation of thicker NPLs.

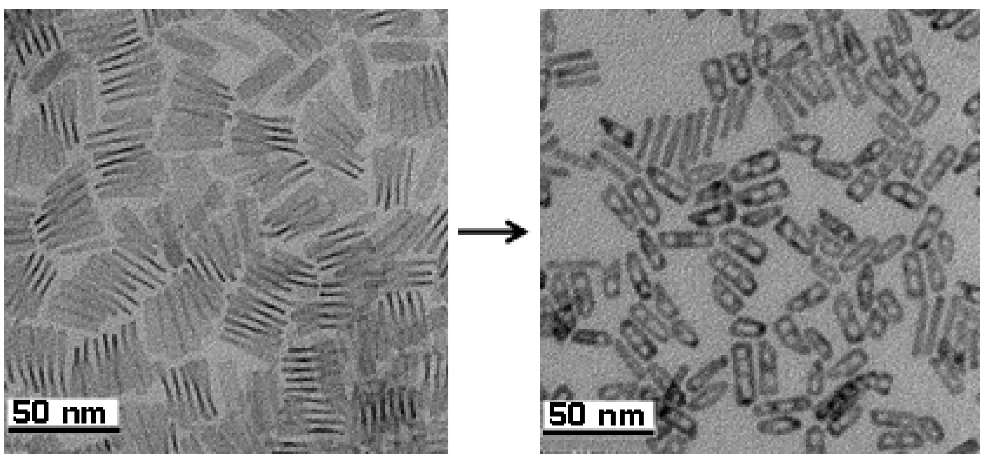
W. Cho, S. Kim, I. Coropceanu, V. Srivastava, B. T. Diroll, A. Hazarika, I. Fedin, G. Galli, R. D. Schaller, D. V. Talapin; *Chem. Mater.* **2018**

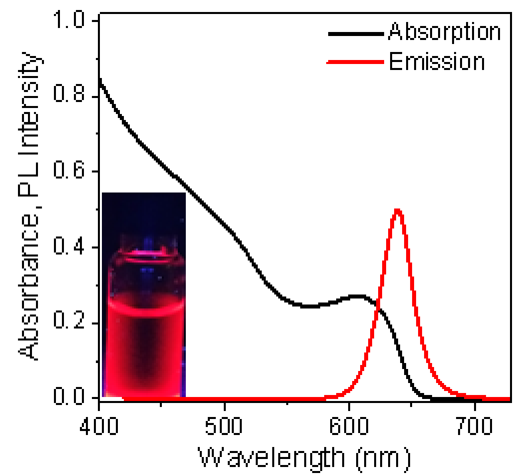
CdSe nanorings and double rings

Perforation of NPLs upon treatment with Se in oleylamine





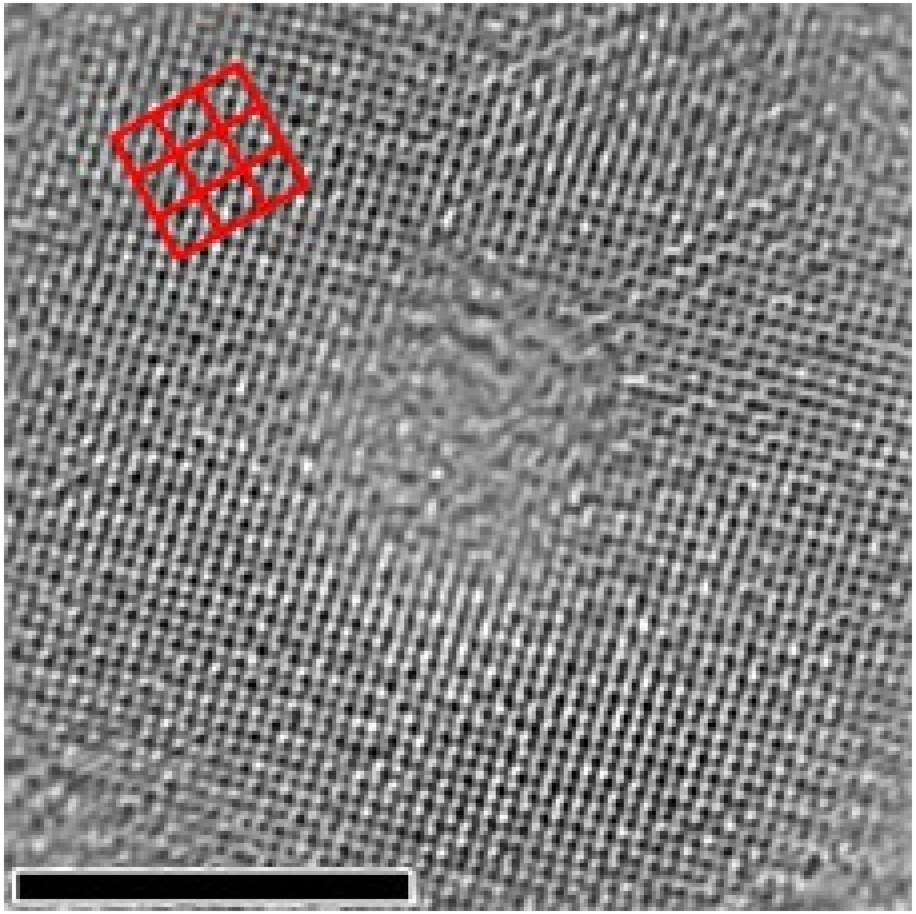




First example of quantum multi-rings

I. Fedin and D. V. Talapin; *JACS* **2016**

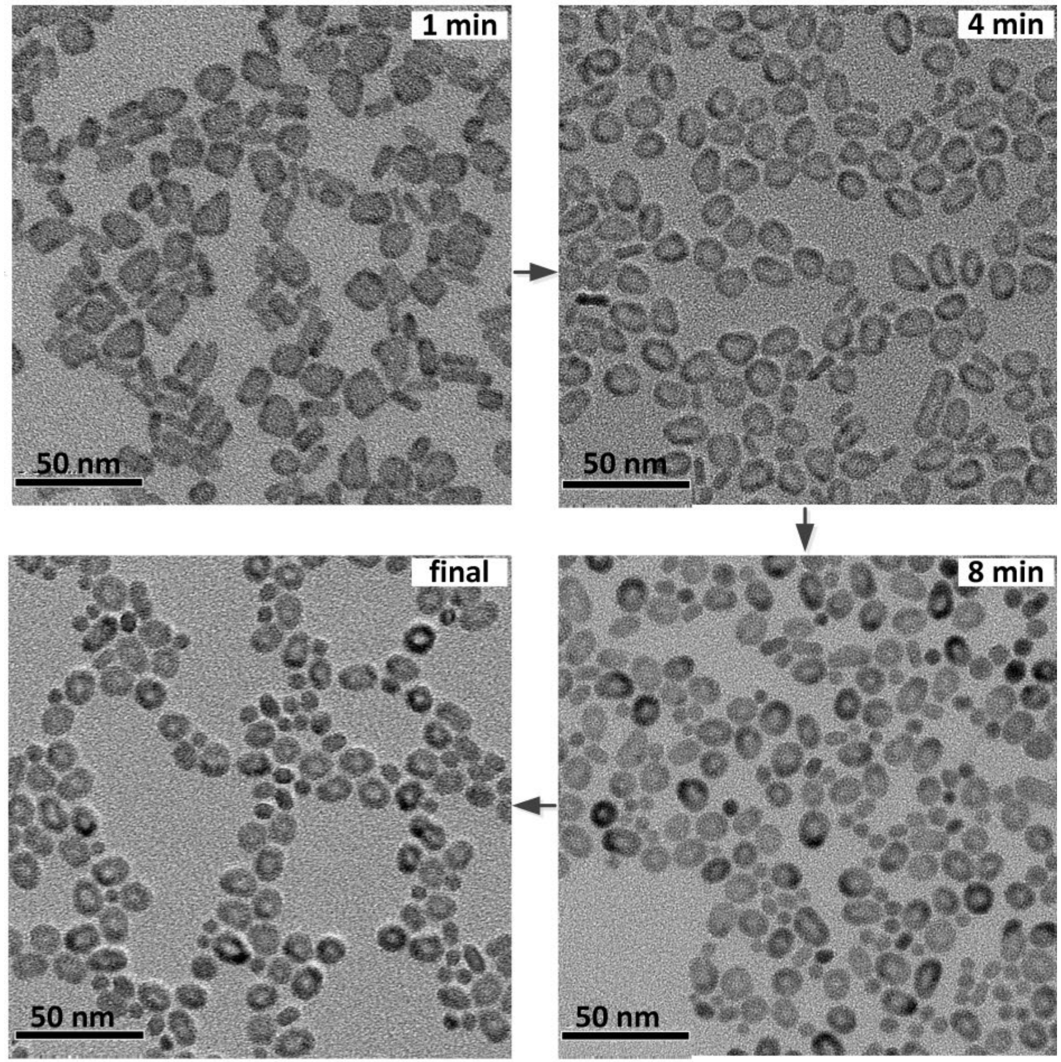
Zinc-blende crystal structure is preserved



Scale bar: 5 nm

Measured $a = 6.1 - 6.2\,\mathring{A}$

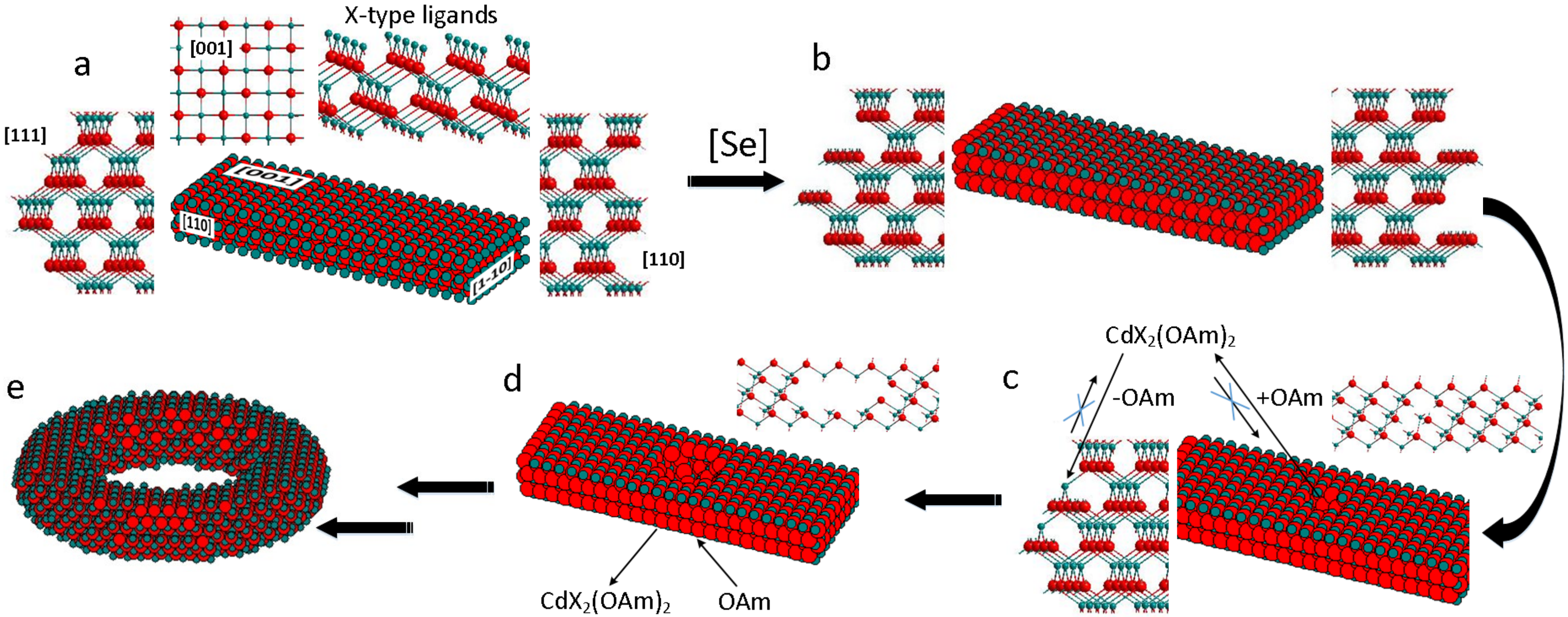
Perforation in progress



What is the mechanism of perforation?

Amine is necessary in the perforation

$RCH_2NH_2 + 2Se \rightarrow RC(Se)NH_2 + H_2Se$

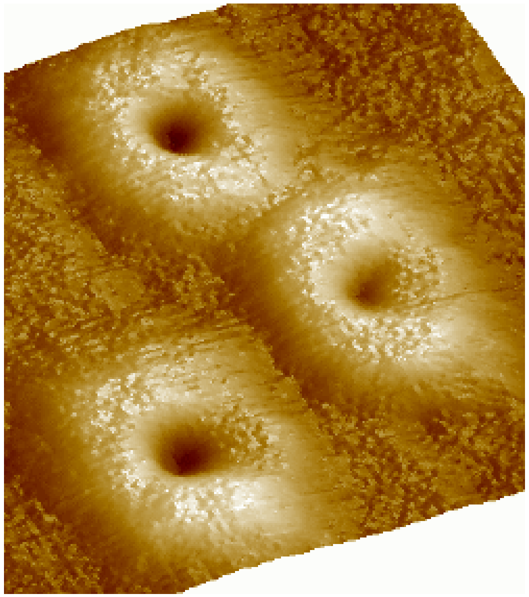


Oleylamine promotes elimination of $Cd(OAc)_2$ as Z-type ligand:

$[CdSe]_{4n}[Cd(CH_3COO)_2]_n(C_{18}H_{35}NH_2)_l \rightarrow [CdSe]_{4n}[Cd(CH_3COO)_2]_{n\text{-}1}(C_{18}H_{35}NH_2)_{l\text{-}2} + Cd(CH_3COO)_2(C_{18}H_{35}NH_2)_2$

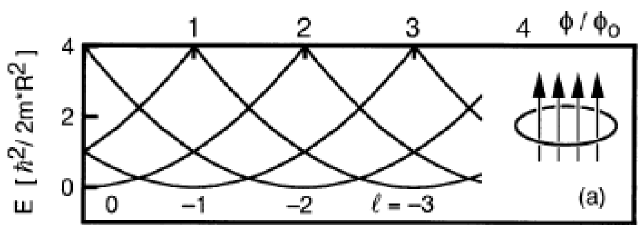
I. Fedin, D. V. Talapin; *JACS* **2016**, *138* (31), 9771 – 9774

Potential applications: Aharonov-Bohm effect

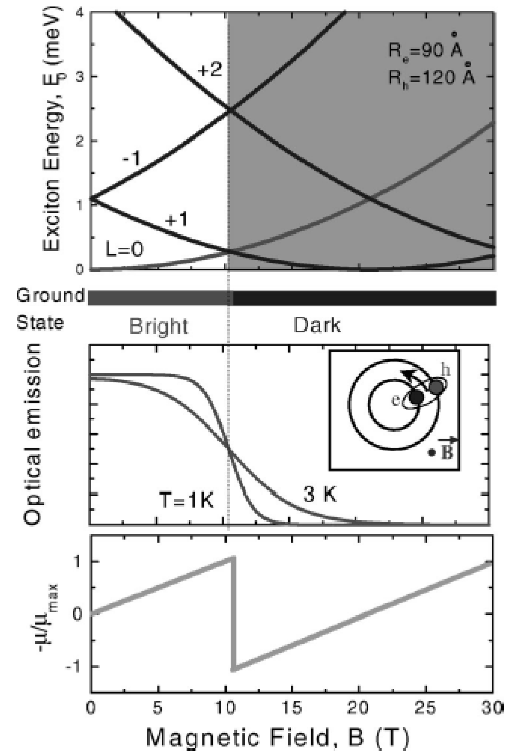


InAs/GaAs

$$E_{exc} = E_g + \frac{\hbar^2}{2m_e R_e^2}\left(L_e + \frac{\Phi_e}{\Phi_0}\right)^2 + \frac{\hbar^2}{2m_h R_h^2}\left(L_h - \frac{\Phi_h}{\Phi_0}\right)^2$$



A. Lorke *et al. Phys. Rev. Lett.* **2000**



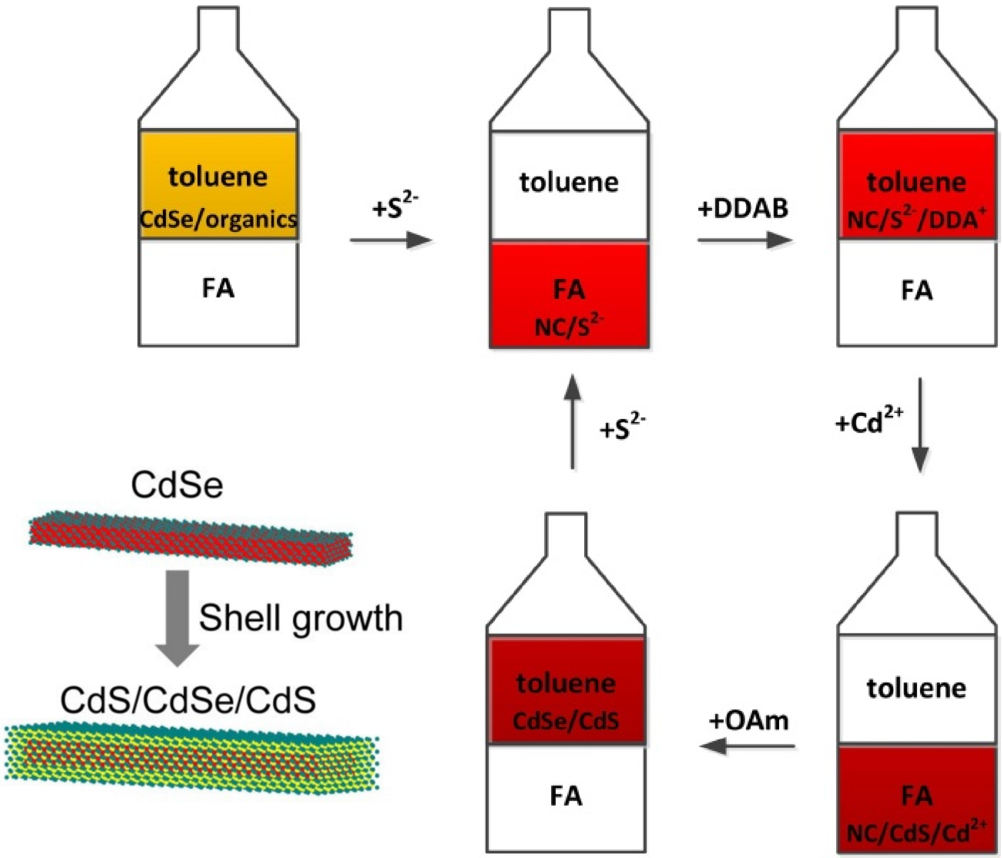
A. Govorov *et al. Phys. Rev. B* **2002**

For our CdSe quantum rings:

$$B = \phi_0 / A = 2.068 \cdot 10^{-15}\,\mathrm{Wb} / 2 \cdot 10^{-17}\,\mathrm{m}^2 \approx 100\,\mathrm{T}$$

50 T to begin observing it

Colloidal atomic layer deposition

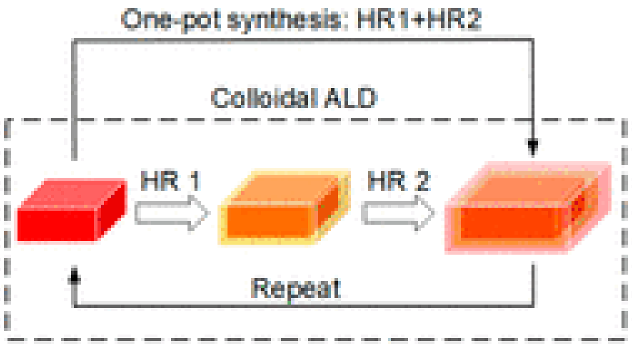


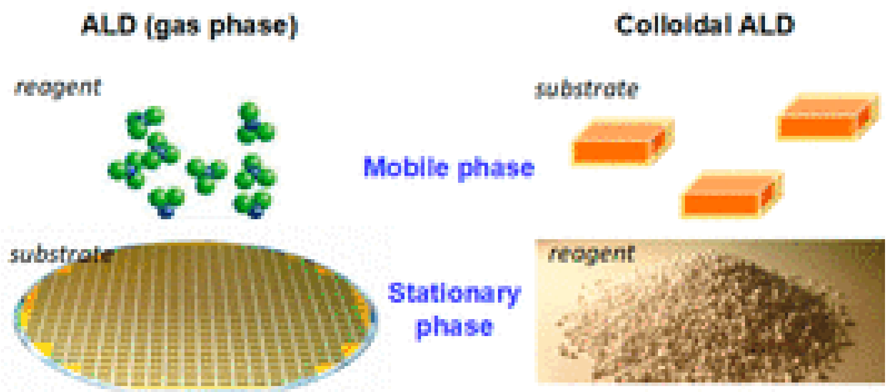
A spectroscopically homogeneous ensemble of CdSe/CdS nanoplatelets

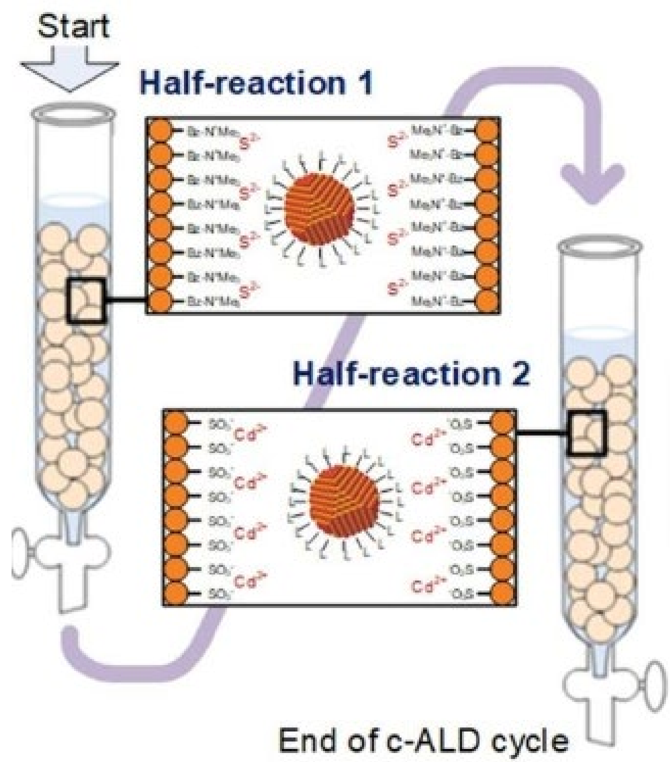
S. Ithurria and D. V. Talapin; *JACS* **2012**

Improvements to *c*-ALD

Swap the stationary and the mobile phases



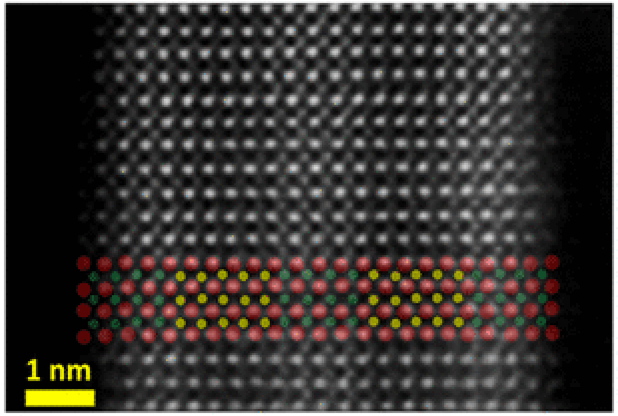


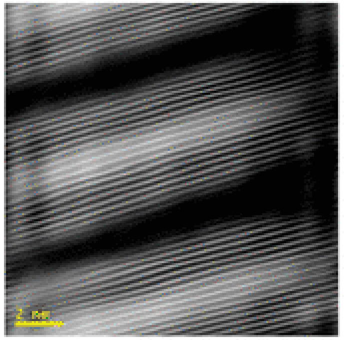


A. Hazarika, I. Fedin, *et al. JACS* **2018**, *141* (34), 13487 – 13496

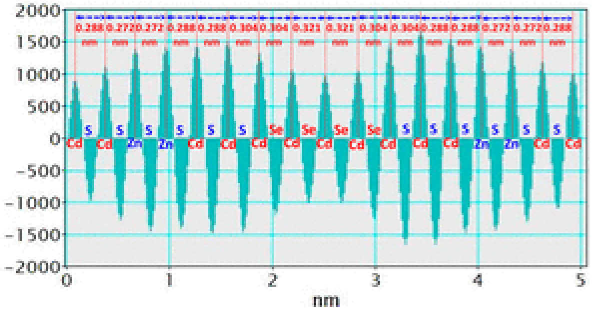
Complex heterostructures

4CdSe/5CdS/4CdSe/5CdS/4CdSe





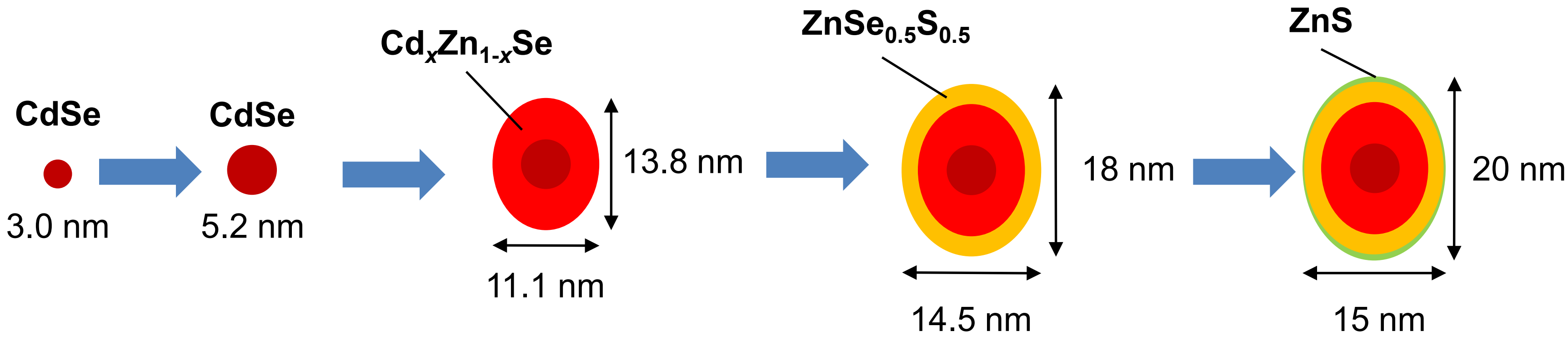
2CdS/2ZnS/2CdS/4CdSe/2CdS/2ZnS/2CdS

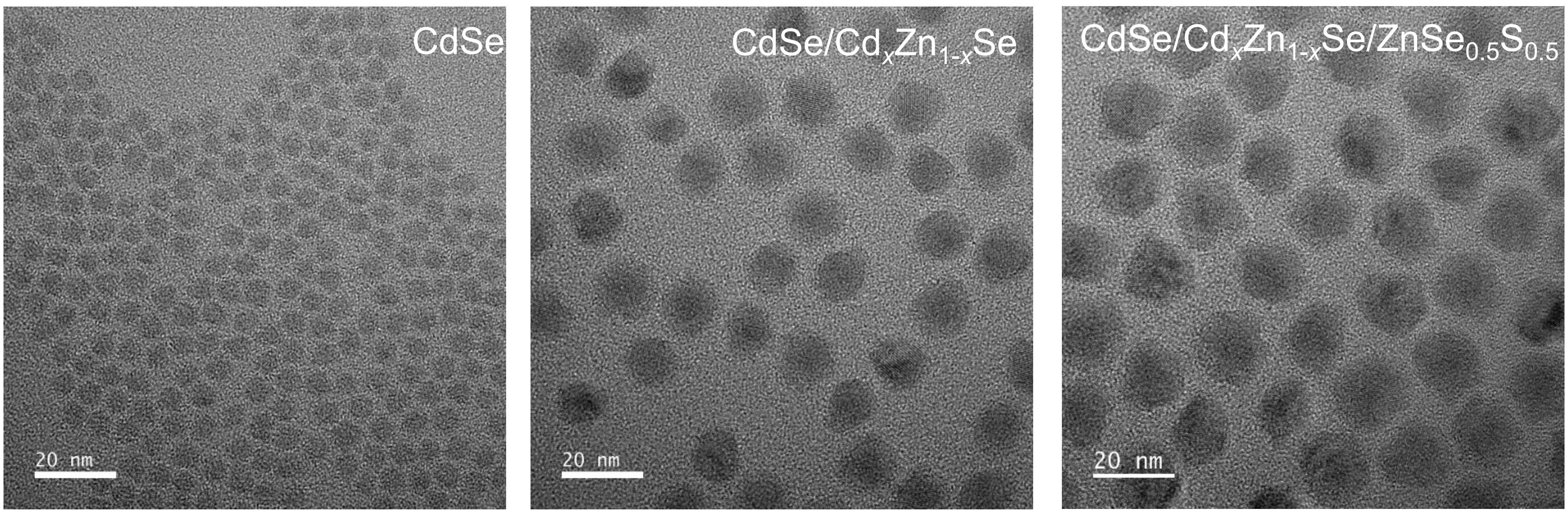


We can produce structures of MBE level of complexity.

A. Hazarika, I. Fedin, *et al. JACS* **2018**, *141* (34), 13487 – 13496

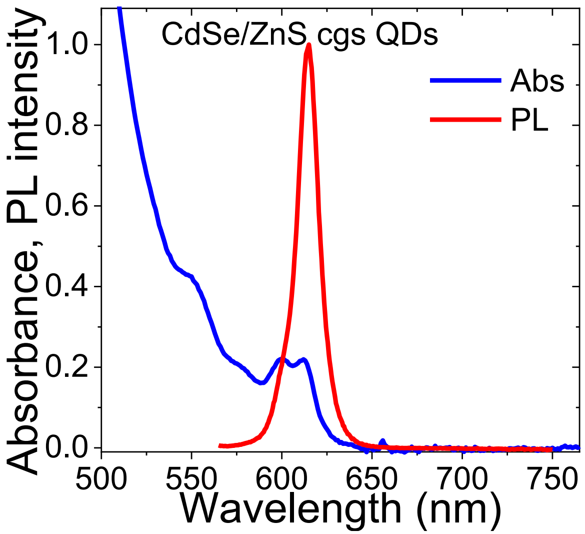
Compositional grading in QDs

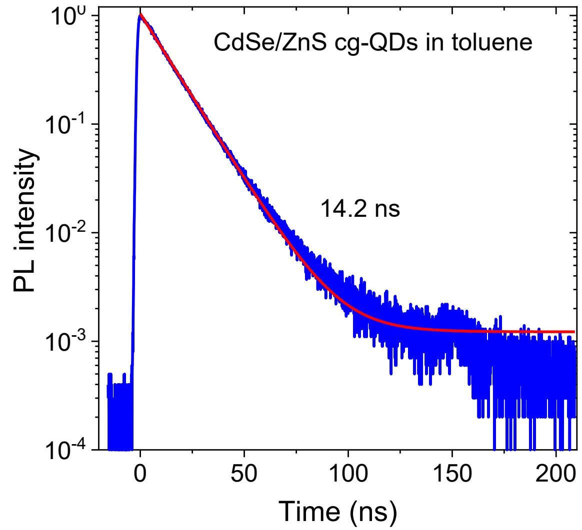


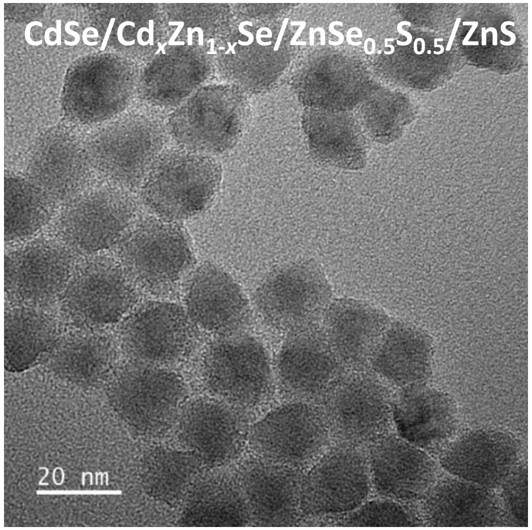


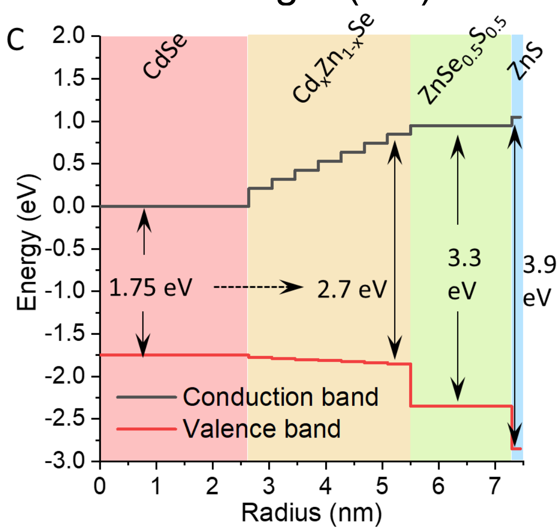
O. Kozlov, Y.-S. Park, J. Roh, I.Fedin, T. Nakotte, *Science* **2019**, *365* (6454), 672 - 675

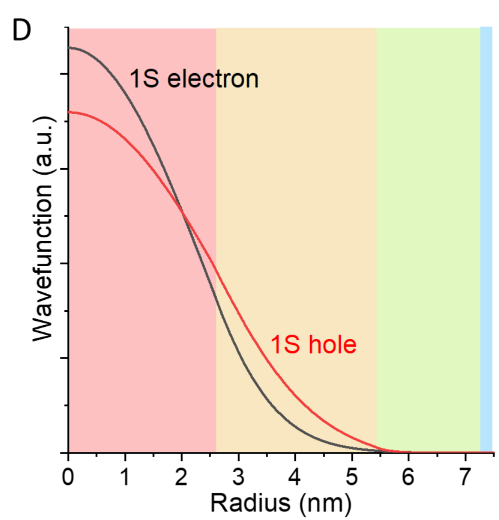
Compositionally graded CdSe/ZnS QDs











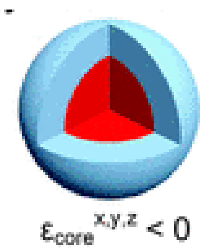
Average x = 0.25

Type-I core-shell structure

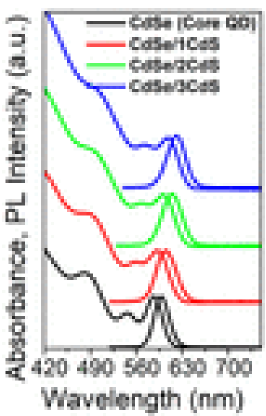
O. Kozlov, Y.-S. Park, J. Roh, I.Fedin, T. Nakotte, *Science* **2019**, *365* (6454), 672 - 675

Effect of strain on optical properties

Ordinary QD core-shells

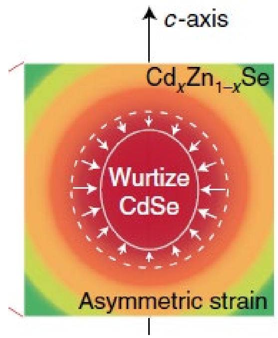


Isotropic (hydrostatic) strain



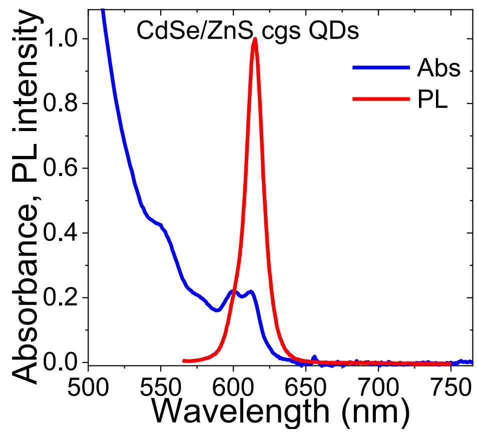
A gradual red shift with a growth of CdS shell

Compositionally graded QDs



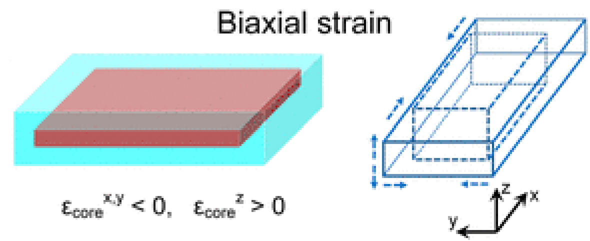
$\varepsilon_{x,y} < \varepsilon_z < 0$

Asymmetric strain

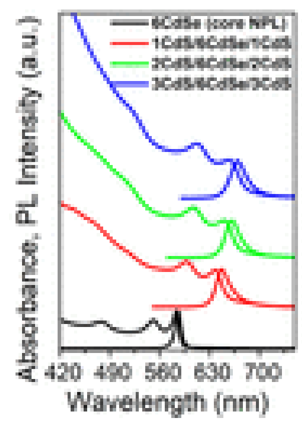


Strain splits light- and heavy-hole excitons.

Nanoplatelet core-shells



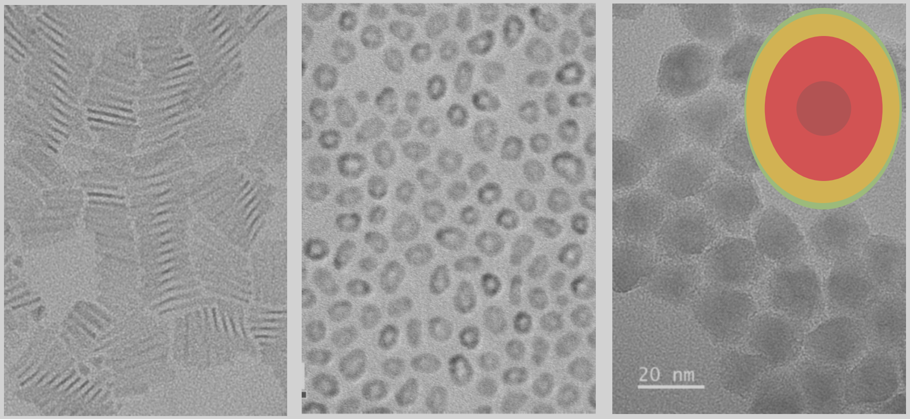
Biaxial strain



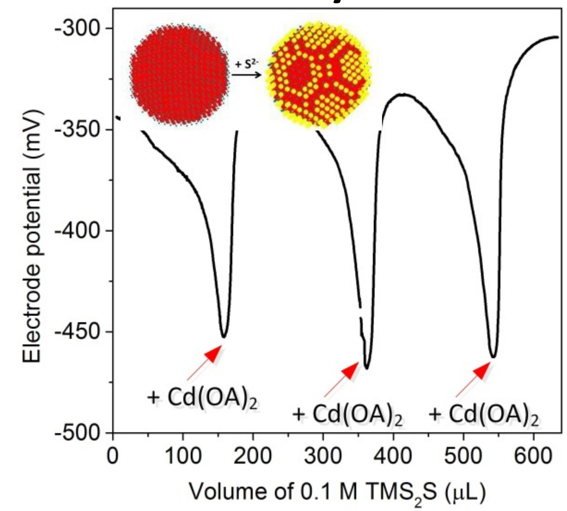
A giant red shift in NPLs after the deposition of the first layer of CdS

Outline

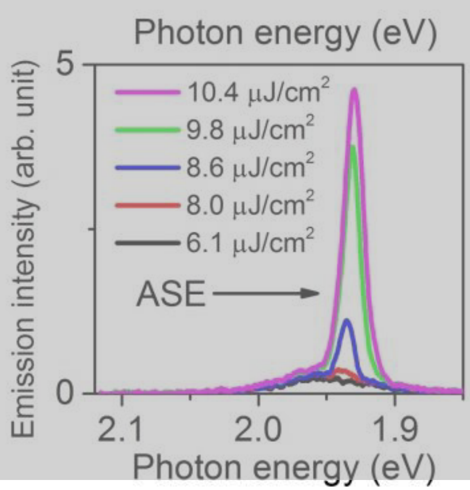
Synthesis of complex heterostructures

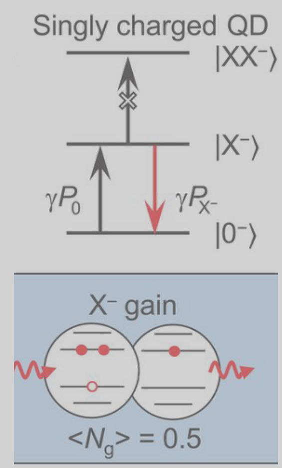


Surface chemistry of colloidal nanocrystals



Photonics of CdSe QDs and NPLs: ASE, lasing, and FRET

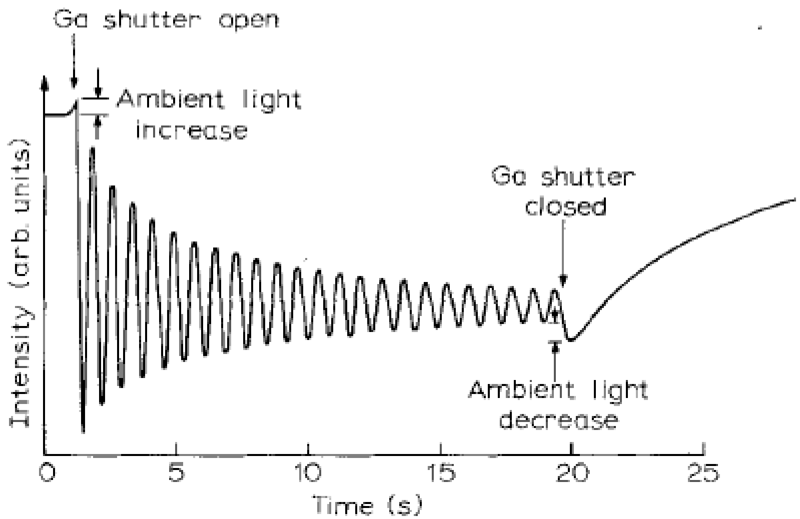




Need for a tool to probe the synthesis *in situ*

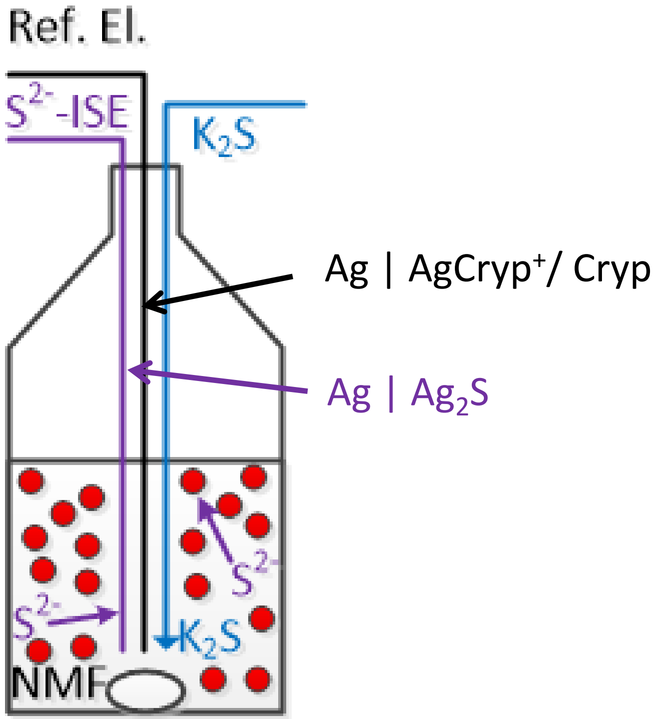
- monitor a ligand exchange or core-shell growth *in situ*
- promptly obtain the feedback from the system
- automate the process

Example from epitaxy: monitoring the deposition of GaAs with RHEED



Appl. Phys. A **1983**, 31, 1 – 8.

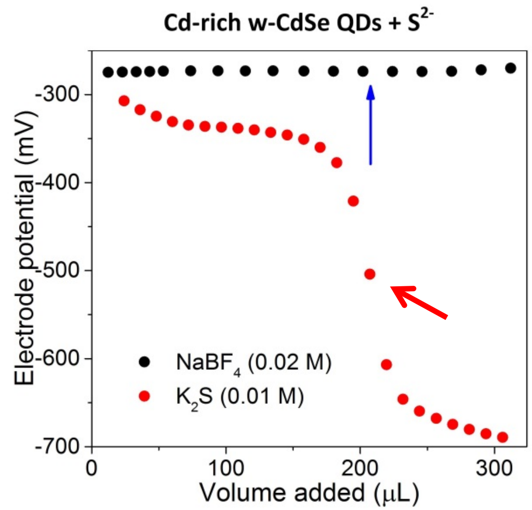
Potentiometry

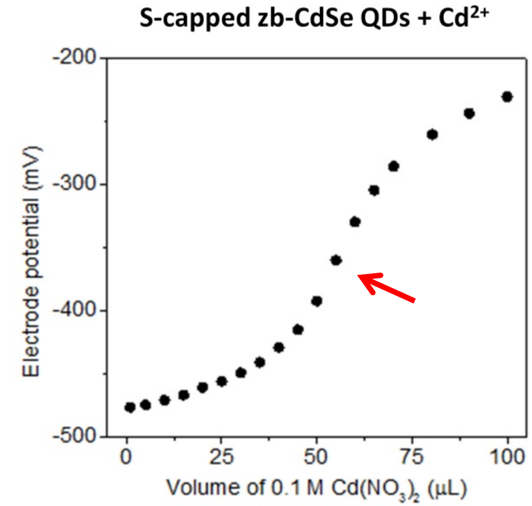


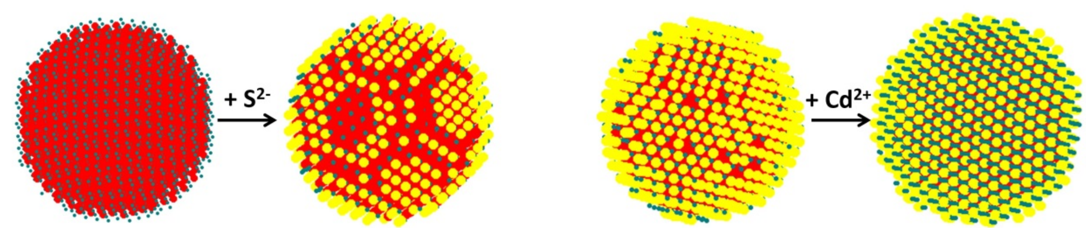
Measured signal: cell voltage

$$V = V^0 - s \cdot \log c_{S^{2-}}$$

Potentiometric titrations







→ growth of a complete shell

Merits:

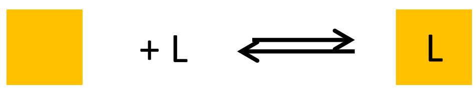
- fast response
- sharp equivalence point

I. Fedin, D. V. Talapin; *JACS* **2014,** *136* (32), 11228

Thermodynamics of ligand adsorption

Langmuir adsorption:

- non-interacting ligands



$1-\theta \qquad c \qquad \theta$

$$K_L = \frac{\theta}{(1-\theta)c}$$ Langmuir isotherm

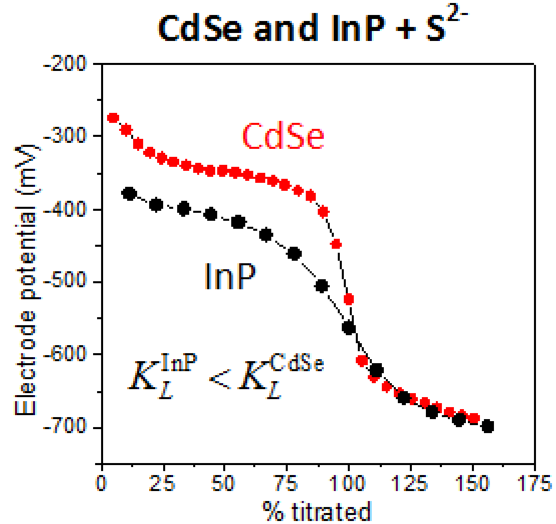
Frumkin-Fowler-Guggenheim isotherm:

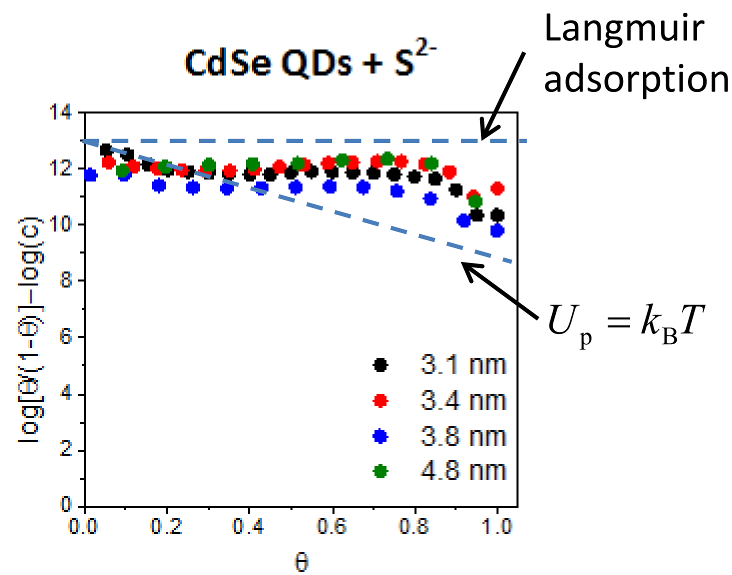
- interacting ligands

$$\frac{\theta}{(1-\theta)c} = K_L \exp\left(-\frac{nU_p\theta}{k_B T}\right) = K_L \exp(\beta\theta)$$

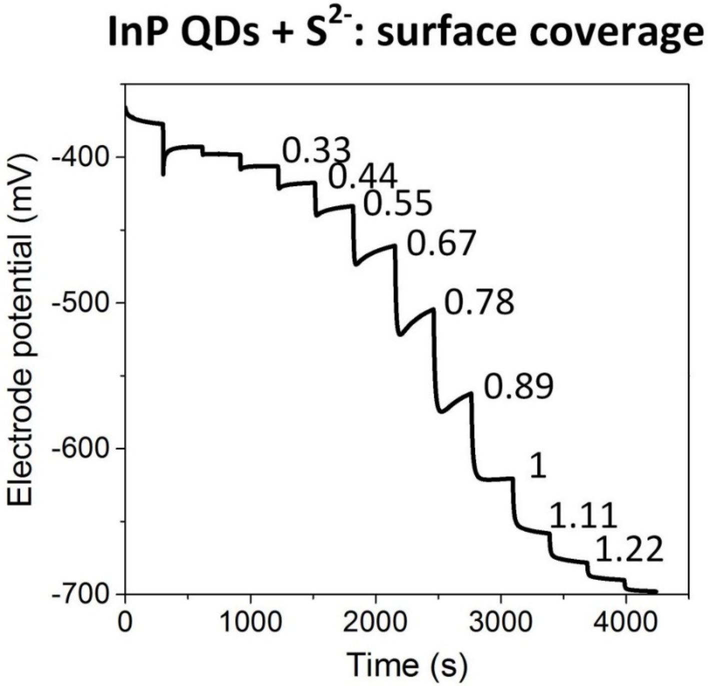
$$\log\frac{\theta}{(1-\theta)c} = \log K_L + \frac{1}{\ln 10}\beta\theta$$

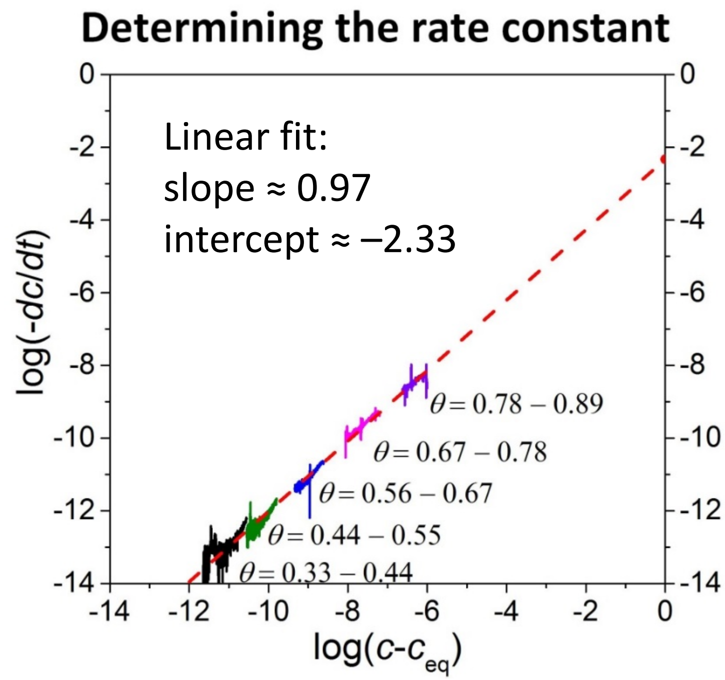
$\beta < 0$ means inter-ligand repulsion





Kinetics of ligand adsorption





The rate of decay of the concentration of S^{2-}:

$$-\frac{dc}{dt} = k \cdot \left(c - c_{eq}\right)^n$$

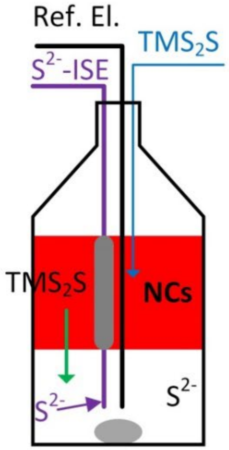
$$\log\left(-\frac{dc}{dt}\right) = \log k + n \cdot \log\left(c - c_{eq}\right)$$

$$n \approx 0.97$$

$$k \approx 4.7 \cdot 10^{-3}\,\mathrm{s}^{-1}$$

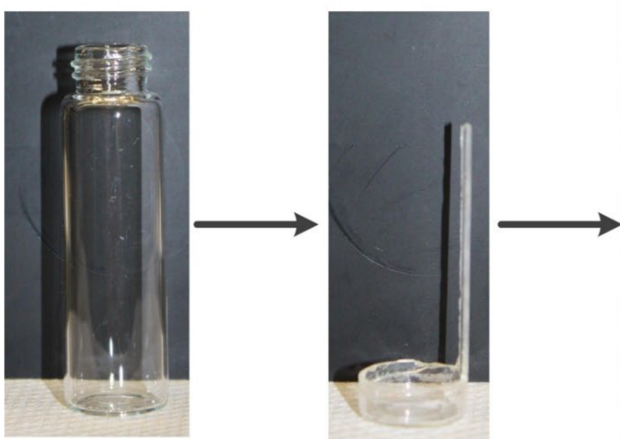
$t_{1/2} \approx 150\,\mathrm{s}$ when S^{2-} is the limiting agent

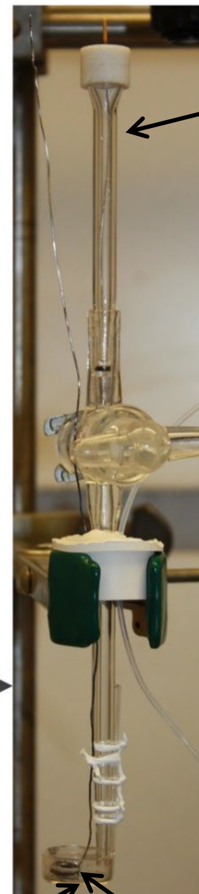
Potentiometry in a non-polar medium



Take electrochemistry outside its comfort zone

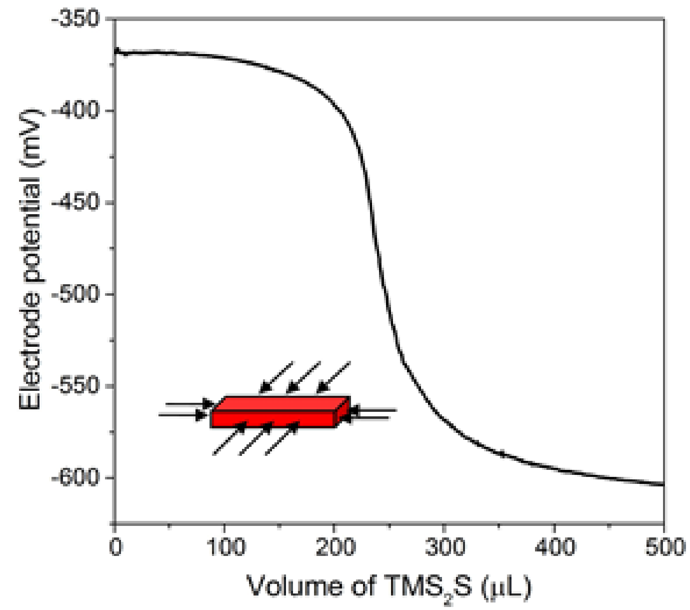
$$\left[S^{2-}\right]_{NMF} = K_{dist}\left[S^{2-}\right]_{ODE}$$





Ag|AgCryp$^+$

CdSe NPLs + TMS$_2$S



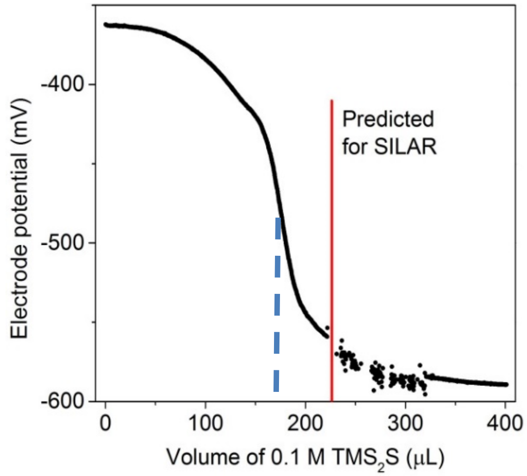
A similar span of electrode potentials as in a polar solvent

NMF

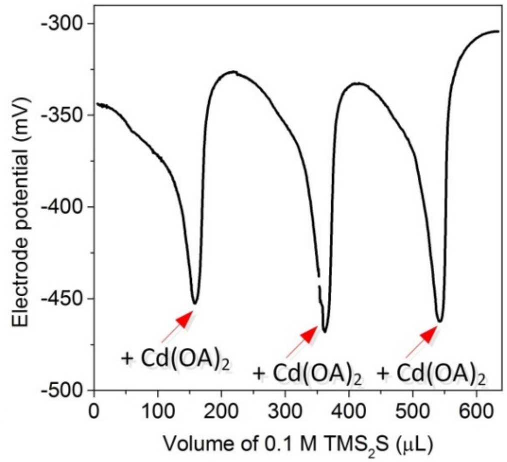
Ag|Ag$_2$S

Controlled core-shell growth in a non-polar medium

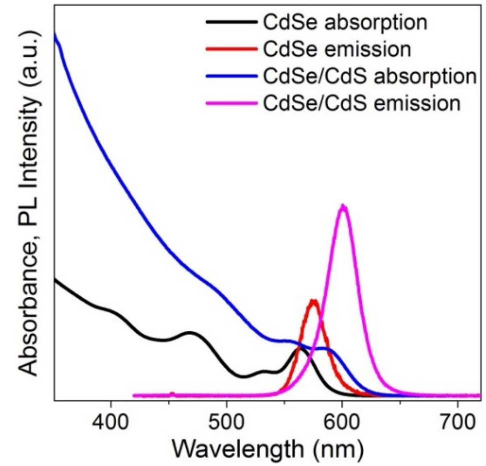
w-CdSe QDs + $[Me_3Si]_2S$

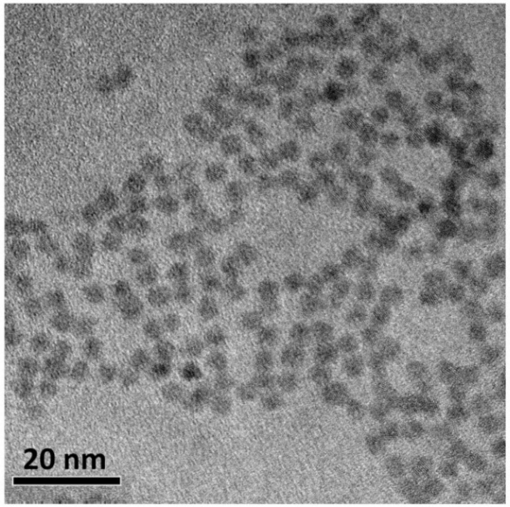


Growth of 3 MLs of CdS

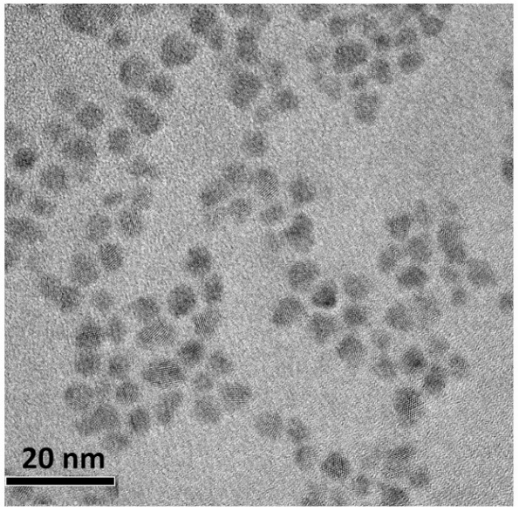


UV-Vis and PL spectra





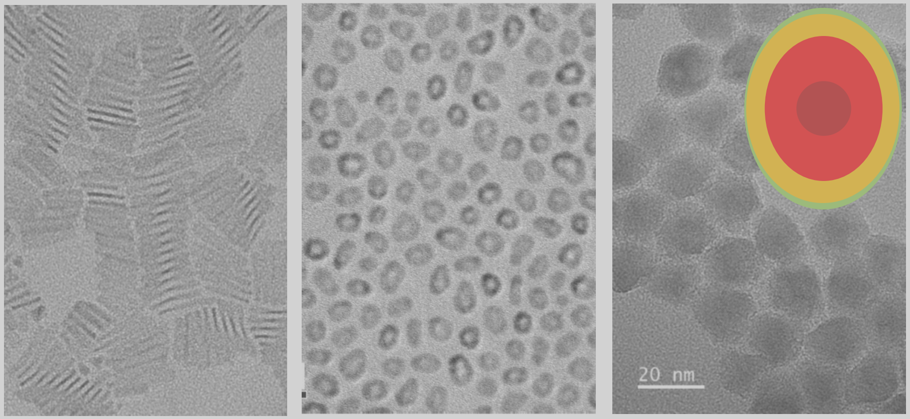
w-CdSe QDs



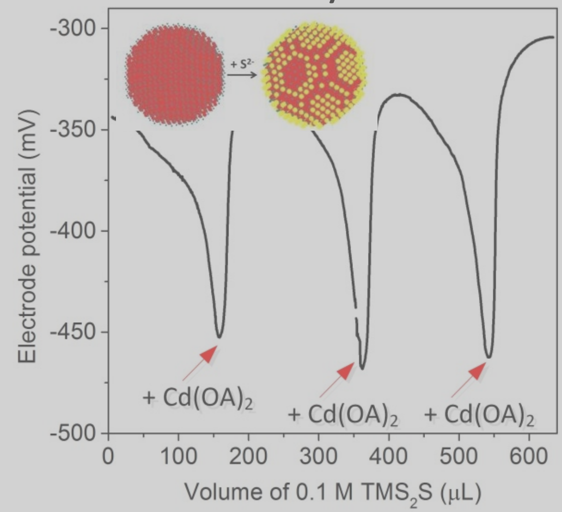
CdSe/CdS QDs

Outline

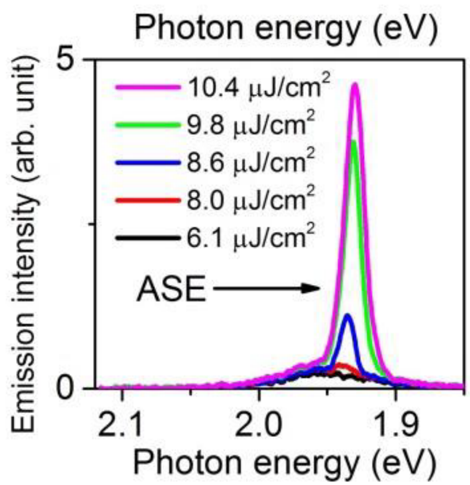
Synthesis of complex heterostructures

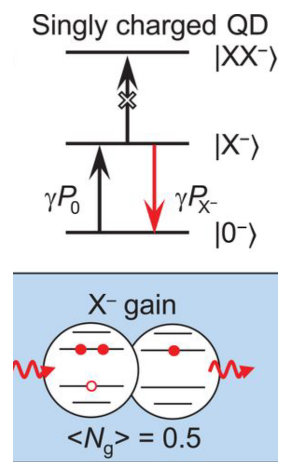


Surface chemistry of colloidal nanocrystals

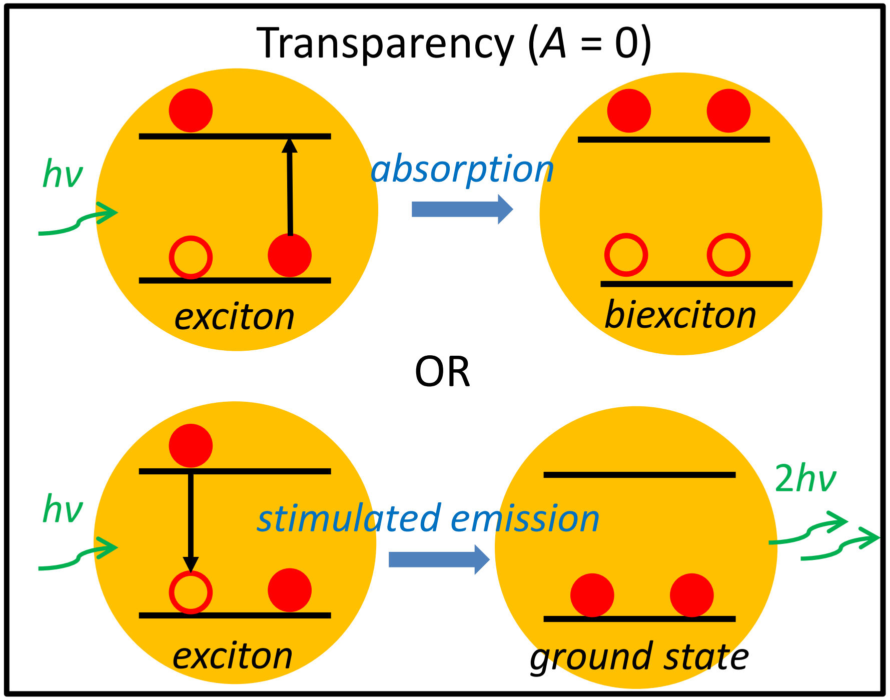


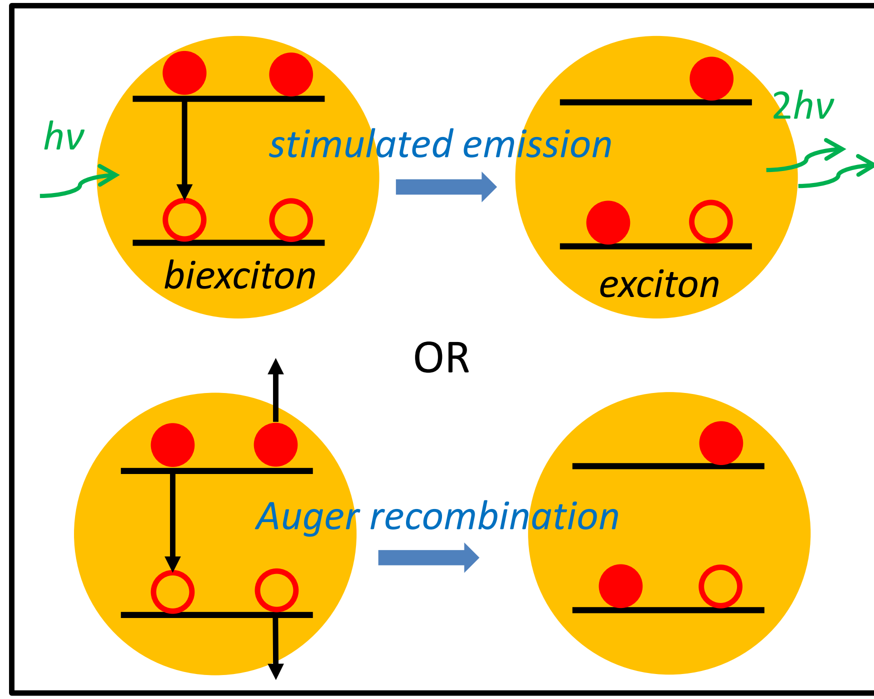
Photonics of CdSe QDs and NPLs: ASE, lasing, and FRET



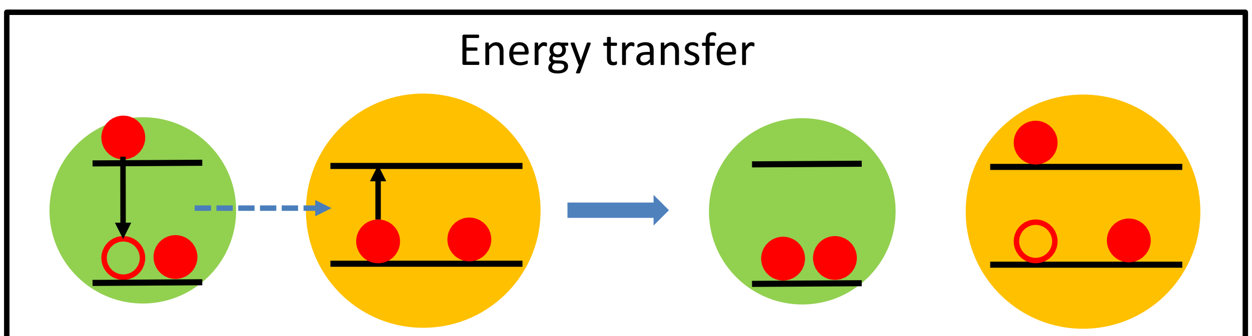


Overview of photophysics in QDs and NPLs



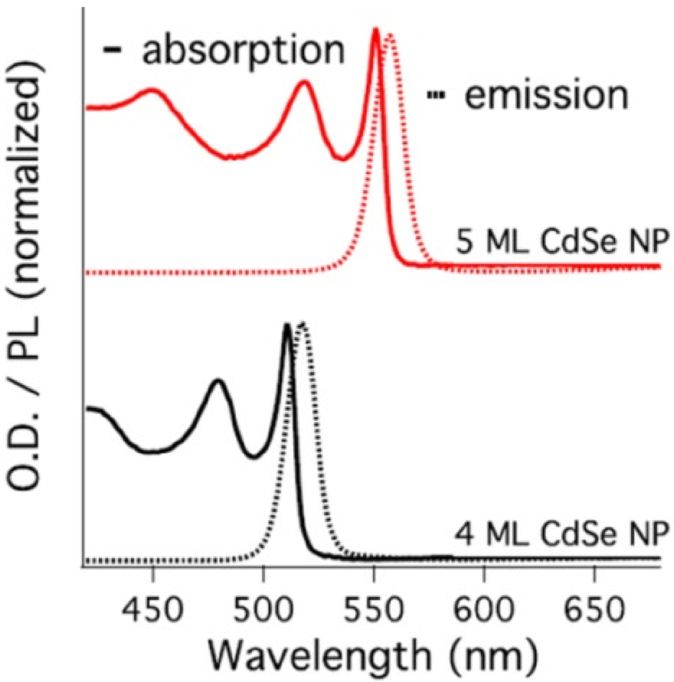


Auger recombination competes with stimulated emission.



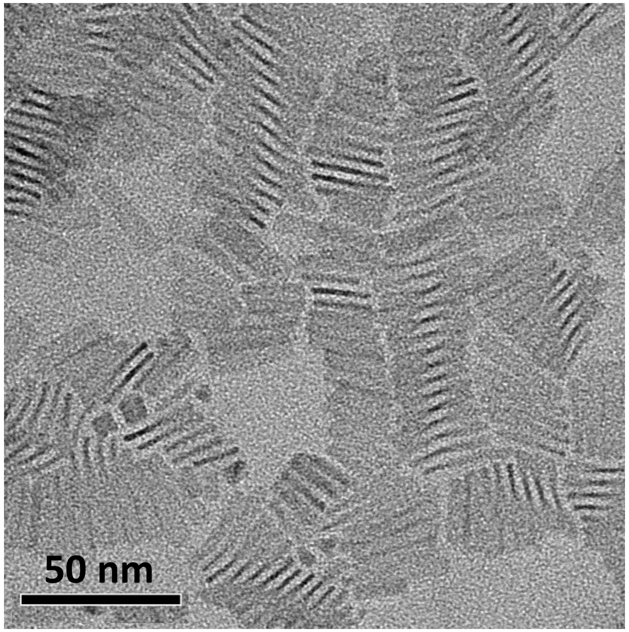
Favorable conditions for energy transfer between NPLs

Spectral overlap



PL of the thinner NPLs aligns with the second exciton (lh–e) of the thicker NPLs.

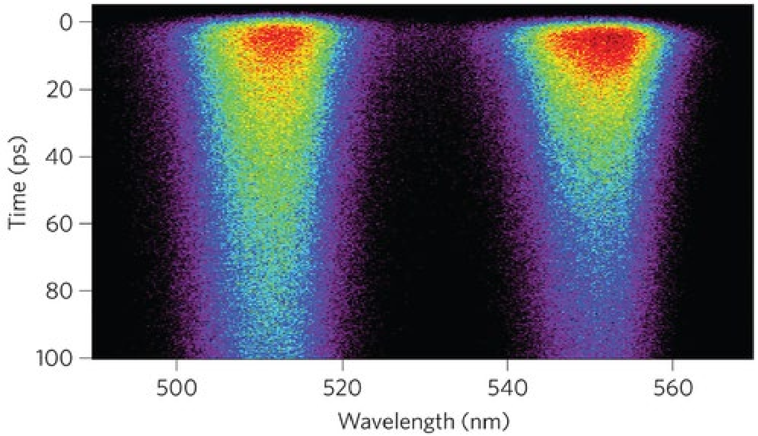
Proximity of donor and acceptor NPLs in a hetero-stack

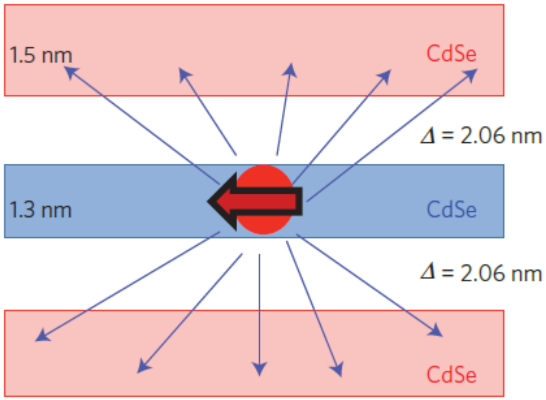


TEM image of heterostacks of 4 ML and 5 ML CdSe NPLs.

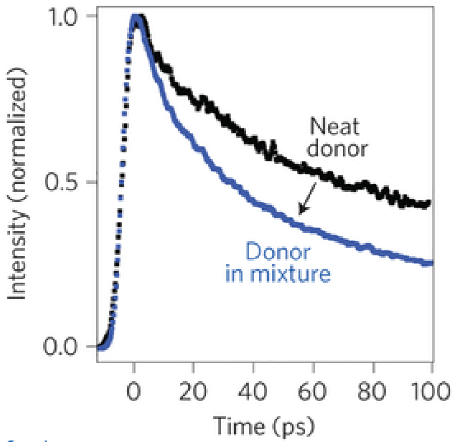
FRET from 4 ML to 5 ML CdSe NPLs

Time-resolved PL of a mix of 4 ML and 5 ML CdSe NPLs

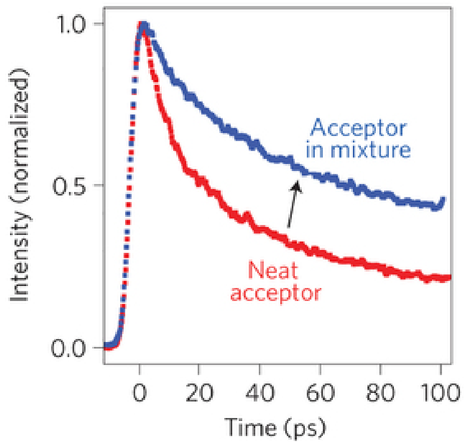




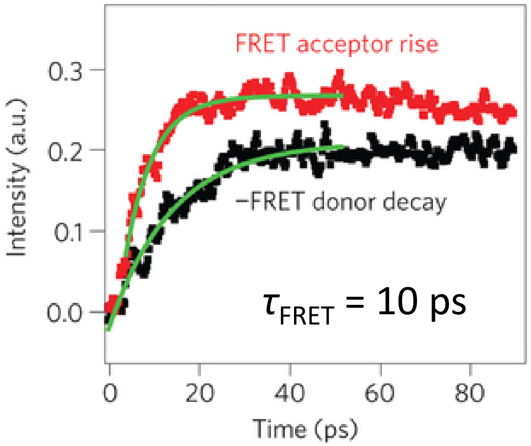
Accelerated donor decay



Decelerated acceptor decay



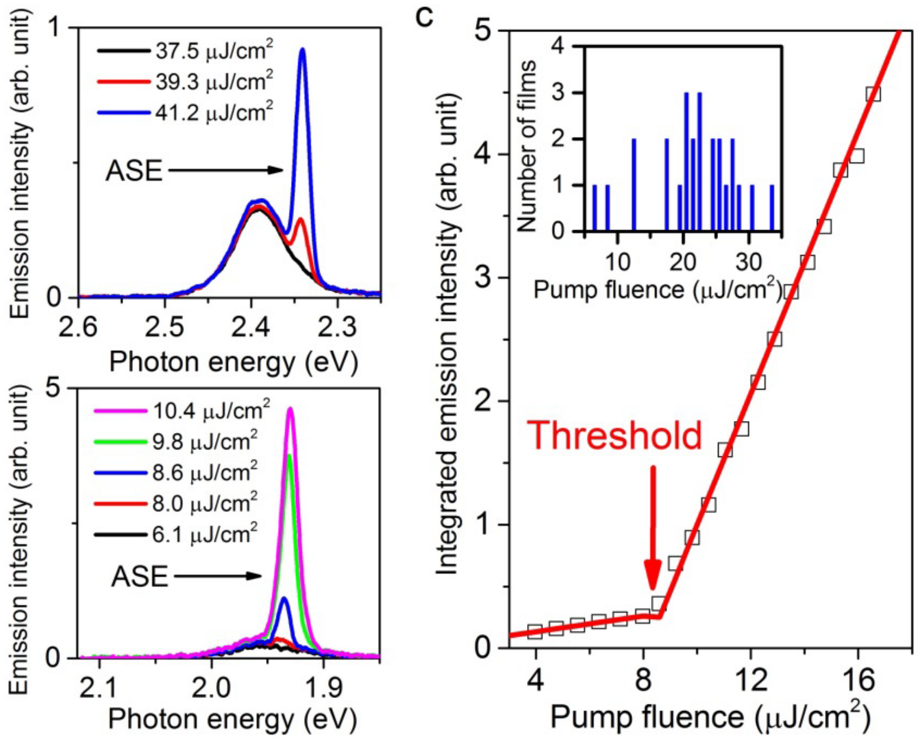
Differenced data



C. Rowland, I. Fedin, *et al*. *Nature Mater.* **2015,** *14*, 484 – 489

Record-low threshold of ASE in CdSe/CdS NPLs

ASE occurs on the red shoulder of PL



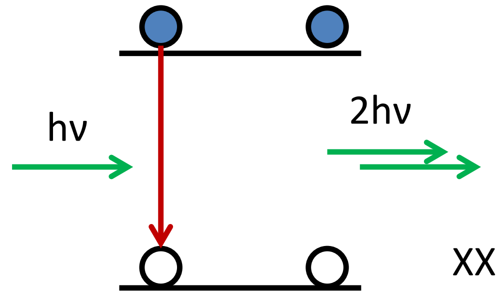
ASE threshold:
Record-low value of 8 μJ/cm²

Absorbed energy = cross-section × fluence

Average # of excitons per NPL = 1.8

at the threshold

Biexcitonic process

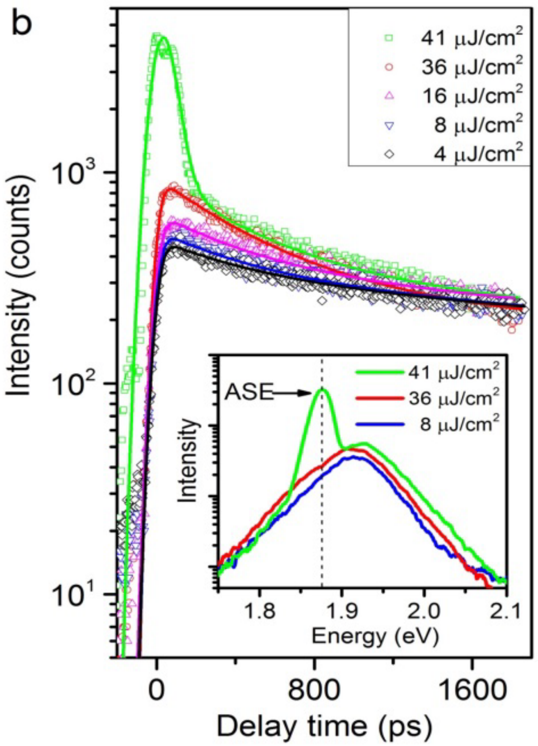


XX + *hv* → X + 2*hv*

C. She,* I. Fedin,* D. S. Dolzhnikov, A. Demortière, R. D. Schaller, M. Pelton, D. V. Talapin; *Nano Lett.* **2014,** *14* (5), 2772-2777 (*equal contribution)

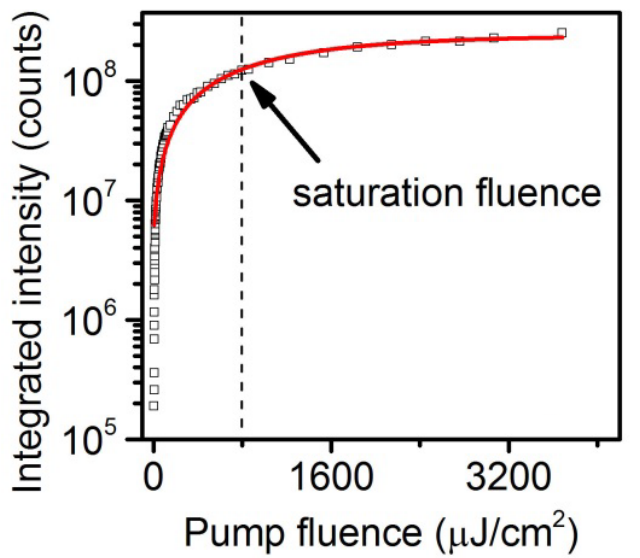
ASE outpaces Auger recombination

PL dynamics of films of CdSe/CdS NPLs by a streak camera



ASE outpaces Auger recombination.

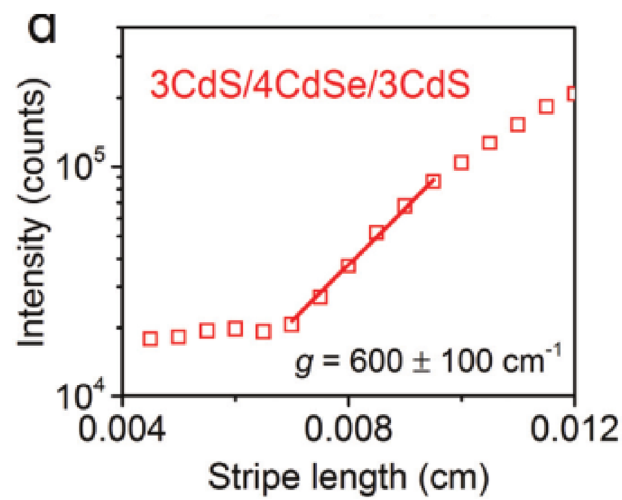
ASE from a film of NPLs



$$E = \frac{\sigma J}{1 + J/J_0} \qquad J_0 = 800\ \mu\mathrm{J}/\mathrm{cm}^2$$

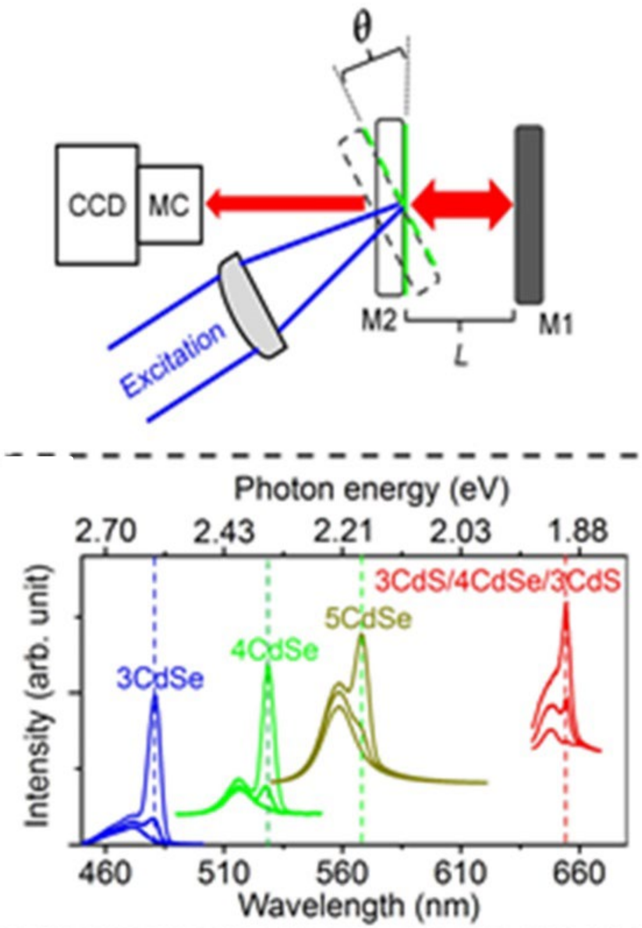
Saturation fluence is two orders of magnitude higher than ASE threshold.

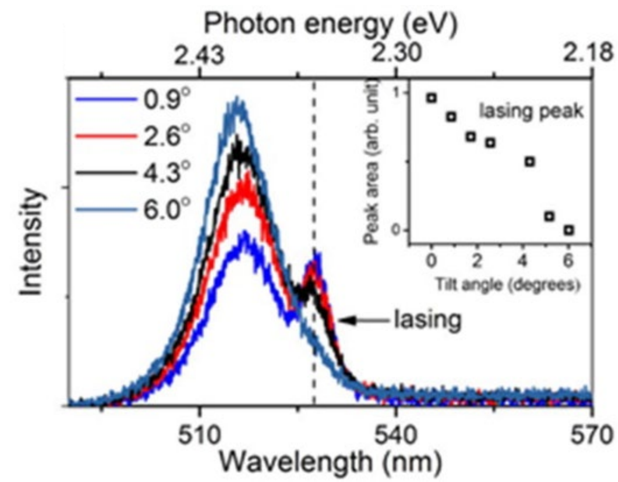
Measuring modal gain



Record-high modal gain of 600 cm^{-1}

Red, yellow, green, and blue laser action



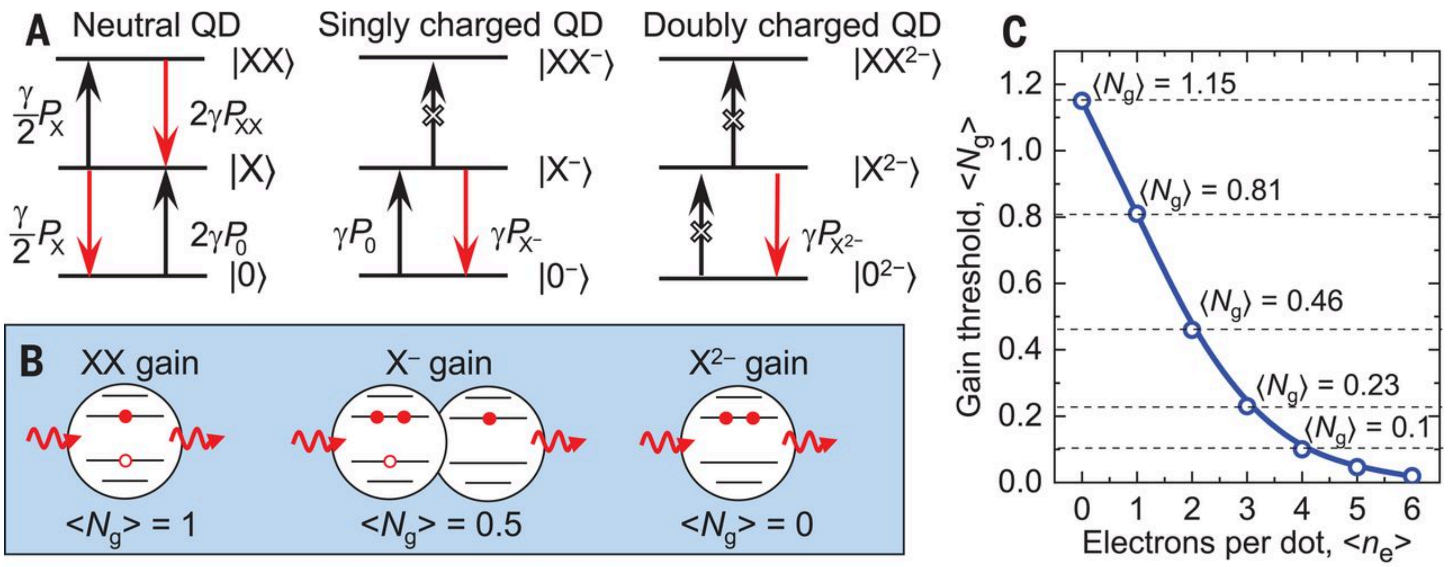


Lasing disappears when the cavity is destroyed by tilting. ASE persists.

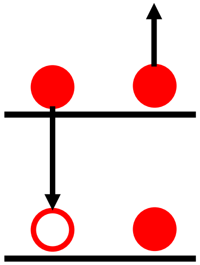
Lasing at 570 nm – a wavelength gap in commercial lasers.

C. She, I. Fedin *et al. ACS Nano* **2015,** *9* (10), 9475-9485

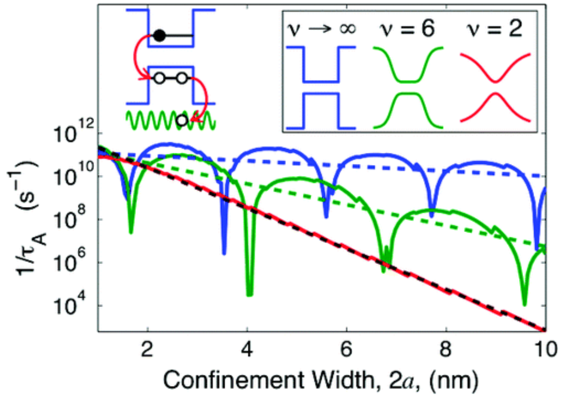
Lower ASE threshold with charging



We expect that charging will lower lasing threshold, but how to handle Auger recombination?



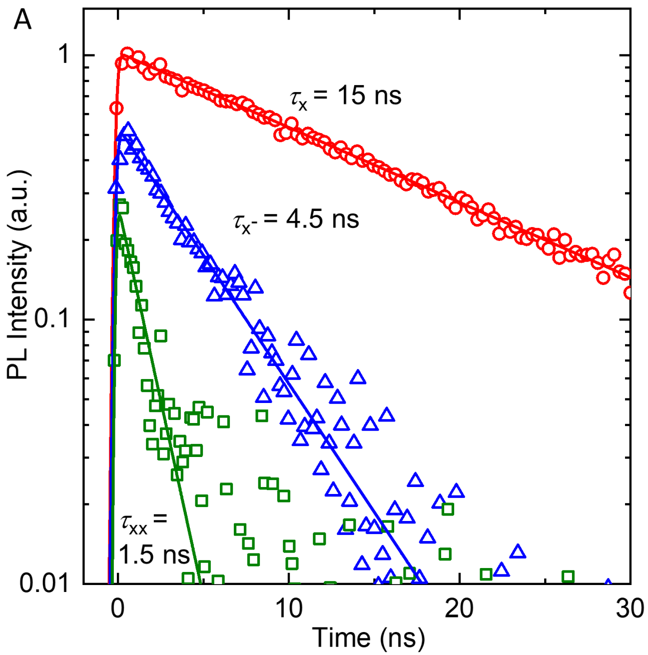
Auger recombination in a negative trion



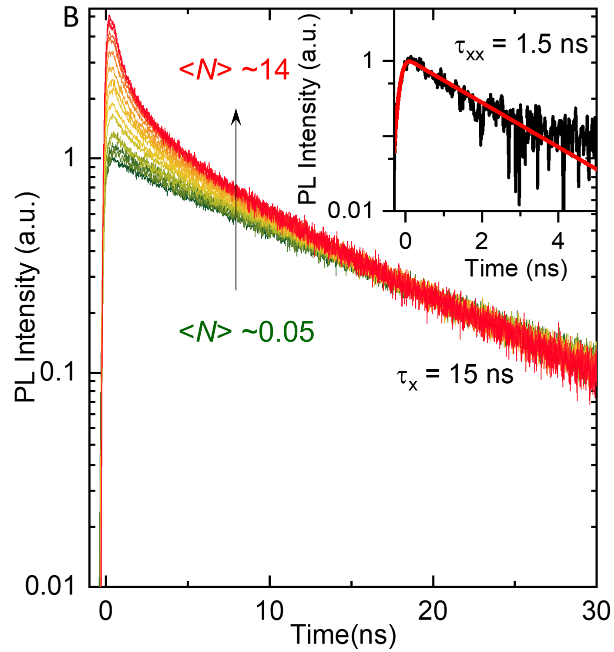
G. Cragg, A. Efros; *Nano Lett.* **2010**

Suppress Auger recombination through compositional grading.

Record-high biexcitonic and trionic quantum yields



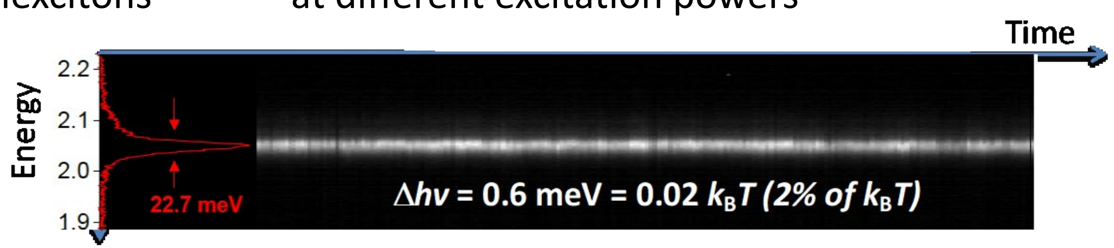
Dynamics of neutral excitons, negative trions, and biexcitons



PL dynamics of CdSe/ZnS cg-QDs at different excitation powers

$$QY_{X^-} = \frac{4.5\text{ ns}}{15\text{ ns}/2} = 60\%$$

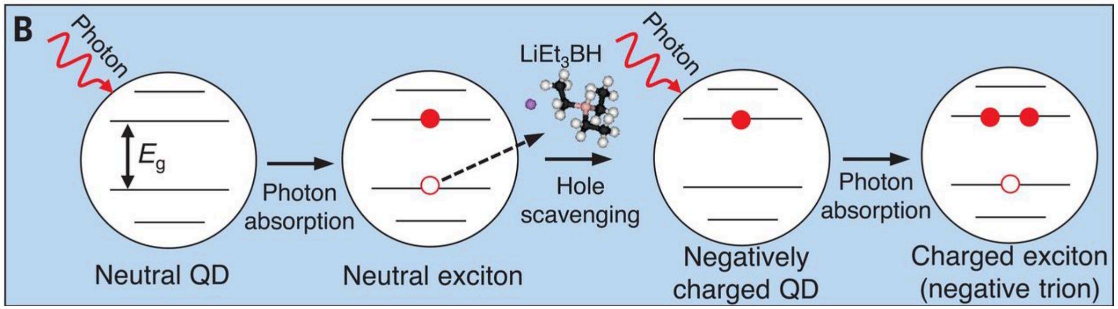
$$QY_{XX} = \frac{1.5\text{ ns}}{15\text{ ns}/4} = 40\%$$

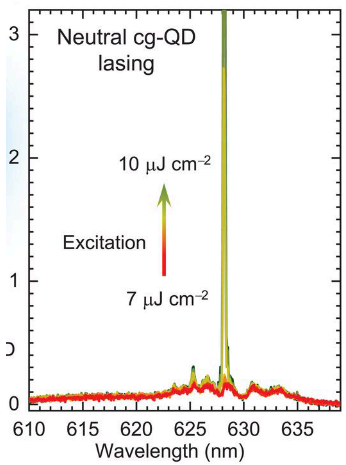


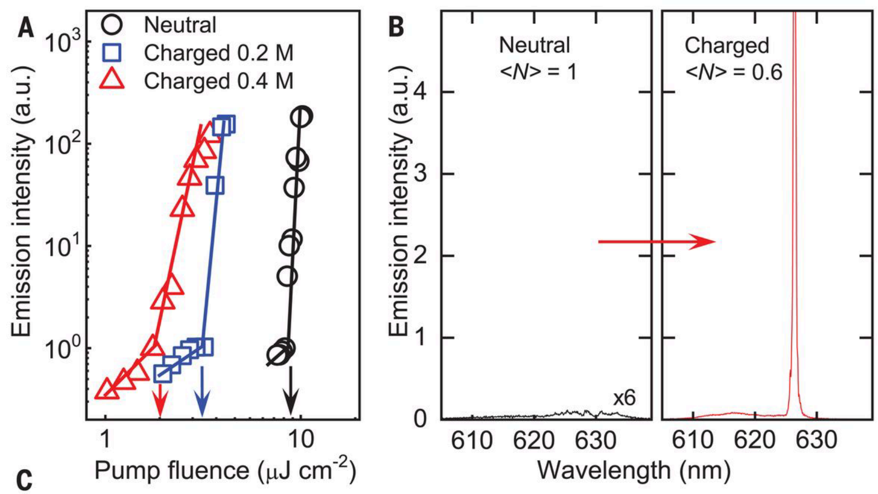
Superior single-dot performance of cg-QDs

Laser action of CdSe/ZnS cg-QDs

Photo-charging CdSe/ZnS QDs with Li superhydride







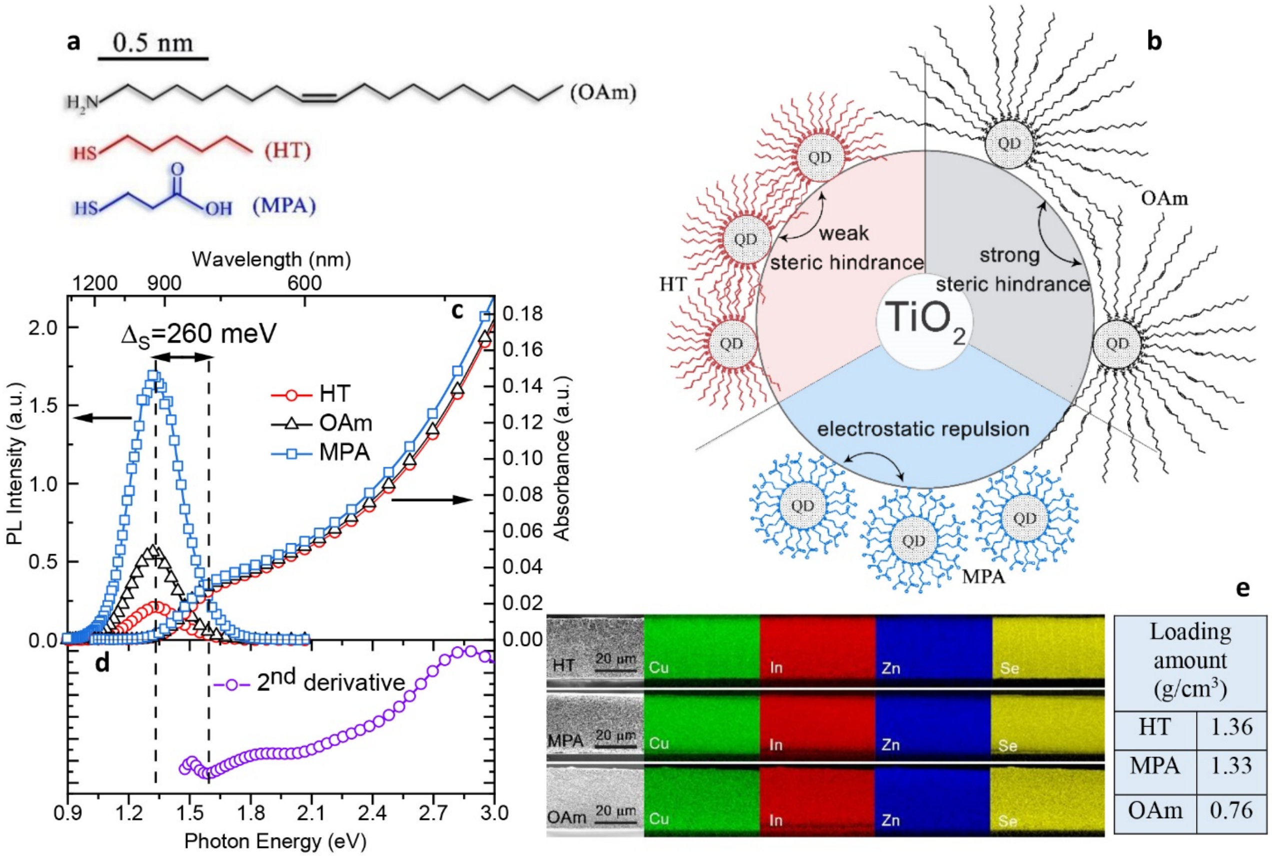
Laser action from neutral CdSe/ZnS cg-QDs

Charging lowers lasing threshold in CdSe/ZnS QDs to sub-excitonic level.

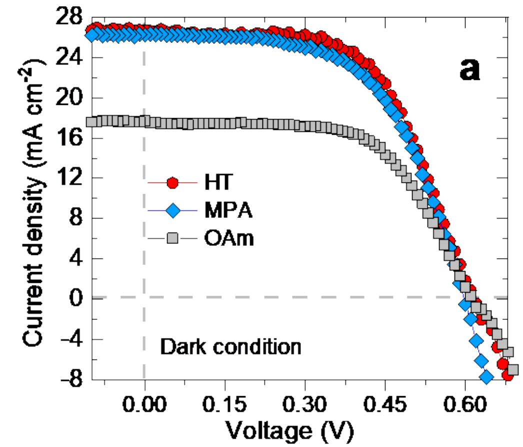
O. Kozlov, Y.-S. Park, J. Roh, I.Fedin, T. Nakotte, *Science* **2019**, *365* (6454), 672 - 675

Illustration: surface chemistry in QD-sensitized PV

$CuInS_2$ QDs in mesoporous TiO_2 as the photoanode material in photovoltaics



Loading amount (g/cm^3)	
HT	1.36
MPA	1.33
OAm	0.76

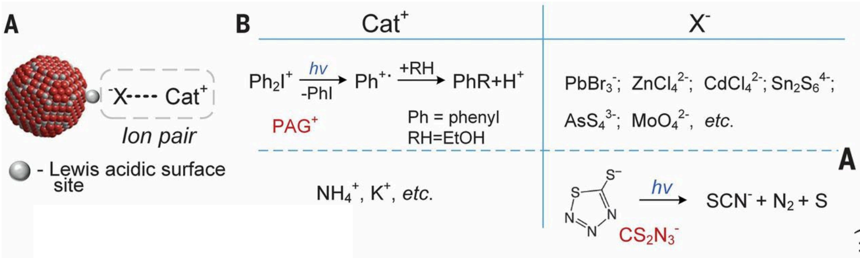


QD loading determines the performance.

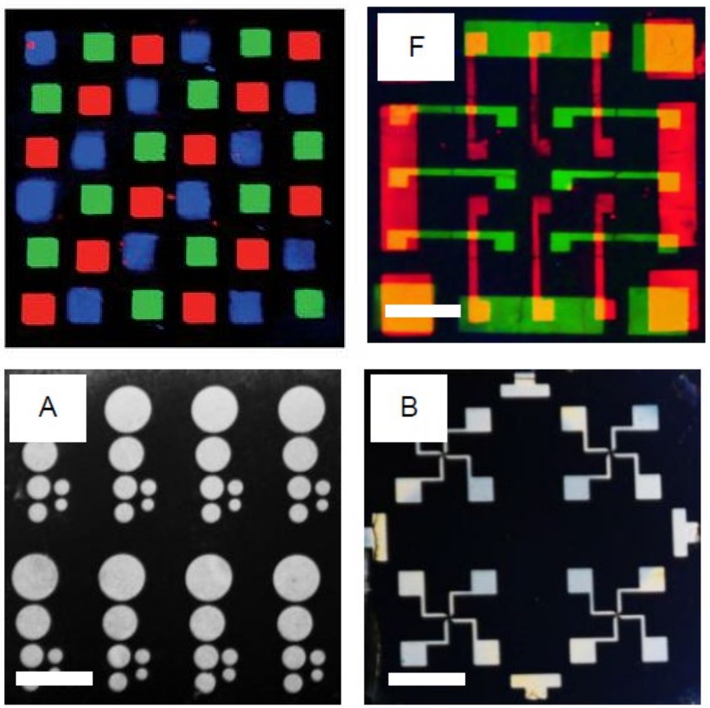
Surface chemistry and inter-ligand interactions determine the photoanode in QD-sensitized solar cells.

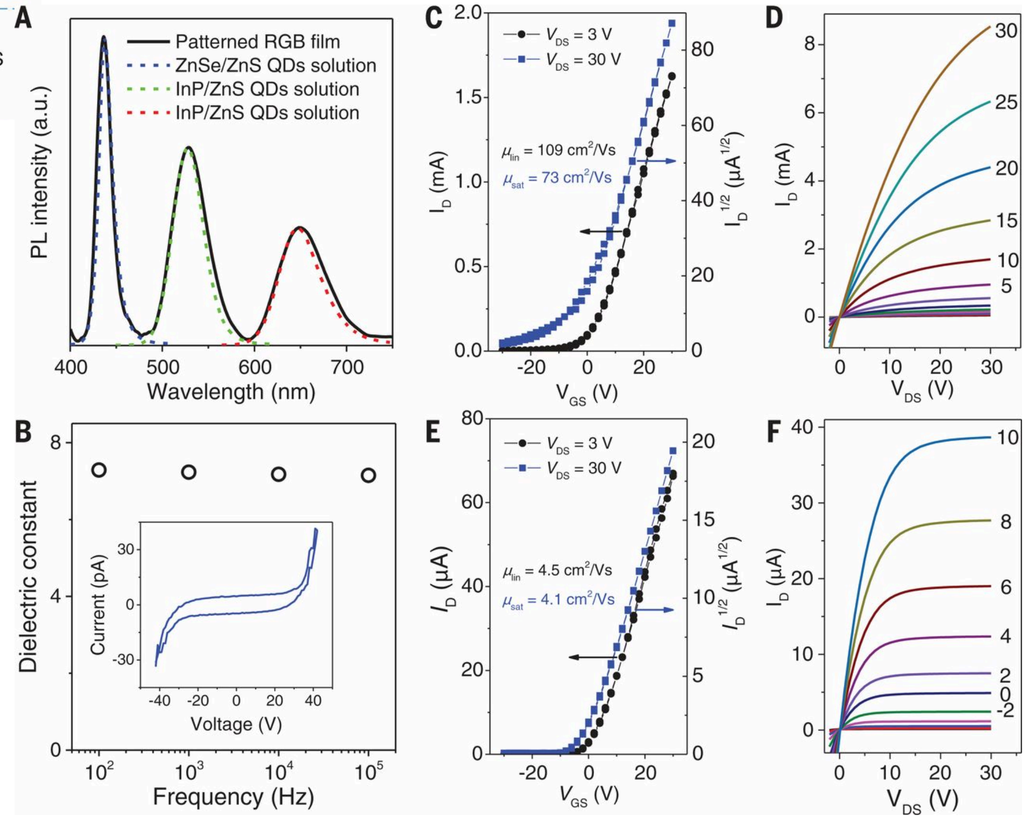
J. Du, R. Singh, I. Fedin, A. Fuhr, V. I. Klimov; *Nat. Energy (final revision)*

Photopatterning



In-Ga-Zn oxide + PAG





Al_2O_3 $\quad$ $CdSe/Na_2Cd_2Se_3 + CdCl_2 + PAG$

Y. Wang, I.Fedin, H. Zhang, D. V. Talapin, *Science* **2017,** *357* (6349), 385 – 388

Summary

- Quantification of the total active surface area of NCs, and thermodynamics and kinetics of ligand adsorption with potentiometry
- Controlled growth of three shells of CdS over CdSe QDs in a non-polar solvent
- Effect of surface chemistry on dye-sensitized PV performance
- First example of colloidal double and triple rings, and discovery of the mechanism of perforation
- Fast energy transfer from CdSe 512 to CdSe 550 NPLs
- Low ASE threshold in CdSe/CdS NPLs of 8 $\mu J/cm^2$, and red, yellow, green, and blue lasing
- Sub-excitonic lasing in compositionally graded QDs
- Excellent performance of photo-patterned semiconductors, dielectrics, and metals

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Dr. Yuanyuan Wang

Dr. Abhijit Hazarika

Dr. Patrick D. Cunningham

Dr. Vishwas Srivastava

Wooje Cho

Dr. Igor Coropceanu

Josh Portner

External collaborators:

Prof. Richard D. Schaller

Prof. Matthew Pelton

Prof. Edo Waks

Dr. Xuedan Ma

Prof. John Lupton